

THE JOURNAL OF GENERAL CHEMISTRY OF THE U.S.S.R

Vol. 21 (1951)

No. 9 (September)

(Publication of the Academy of Sciences of the U.S.S.R.)

IN ENGLISH TRANSLATION

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CONSULTANTS BUREAU

152 West 42nd Street
New York 18, N.Y.

Printed in Great Britain

Annual subscription, \$95.00
Single issue, 12.00

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RESEARCH ON ISOPOLYMOLYBDATES OF THE ALKALI ELEMENTS
BY THE HYDRATION METHOD

Vikt. I. Spitsyn and I. M. Kuleshov

The literature contains numerous references to acid molybdates of the alkali elements, described chiefly by studying the phase diagrams of systems of the $\text{Me}_2\text{MoO}_4\text{-MoO}_3$ type. Di-, tri-, and tetramolybdates of lithium have been found [1]. Sodium forms a dimolybdate [2], as well as, possibly, a tri- and tetramolybdate [1]. Opinions differ regarding the isopolymolybdates of potassium. Amadori [3] used the method of thermal analysis to establish the fact that di-, tri-, and tetramolybdates of potassium are formed in the $\text{K}_2\text{MoO}_4\text{-MoO}_3$ system. Hoermann [1] found nothing but the trimolybdate. Spitsyn and Kuleshov [4] confirmed the formation of potassium di-, tri-, and tetramolybdates, and demonstrated the likelihood that potassium hexa- and octamolybdates also exist. The same authors discovered analogous compounds in the $\text{Rb}_2\text{MoO}_4\text{-MoO}_3$ system. In contrast to the preceding systems, the $\text{Cs}_2\text{MoO}_4\text{-MoO}_3$ system has no dimolybdate.

As a rule, isopolymolybdates have not been isolated from their melts for preparative purposes hitherto, nor have they been investigated individually. The only paper on this topic is that by Svanberg and Struve [5], who isolated sodium dimolybdate from solution after treating a $\text{Na}_2\text{O} \cdot 2\text{MoO}_3$ alloy with water.

One of the present authors [6] has shown that mixtures of acid wolframate may be separated by making use of the different rates at which their components react with water. Acid wolframates containing a low percentage of tungstic anhydride (such as $\text{Na}_2\text{W}_2\text{O}_7$) are hydrated fairly readily in the cold, and even more rapidly when boiled, being converted into a mixture of soluble wolframates: usually the parawolframate and the normal wolframate. More highly acid compounds, such as the tri-, and tetrawolframates, are hydrated more slowly. They are only slightly soluble, even when finely pulverized preparations are heated. Here, again, the solution process consists of the hydration of the anhydrous isopoly compounds, converting them into aquo-poly-compounds, chiefly metawolframates.

The differences in the behavior of the isopolywolframates in water, depending upon their composition, the fineness of grind, and the processing temperature, make it possible to make out a chemical plan for investigating systems of the $\text{Me}_2\text{WO}_4\text{-WO}_3$ type.

We employed the hydration method described above to investigate alloys of acid molybdates in order to secure pure individual isopoly compounds. At the same time we were interested in settling the question whether the compounds detected by the method of thermal analysis during the initial crystallization of the alloys exist at ordinary temperatures or not.

TABLE 1

Composition and appearance of Alloys of Acid Molybdates of the Alkali Elements

Composition of alloy	MoO ₃		Appearance
	Found	Calculated	
Li ₂ O·2MoO ₃ ..	93.61	90.99	Pale-yellow acicular crystals
Li ₂ O·3MoO ₃ ..	93.50	93.53	Light-gray needles
Li ₂ O·4MoO ₃ ..	95.00	95.06	Lustrous gray prisms
Li ₂ O·5MoO ₃ ..	95.85	95.93	Amber-yellow prisms
Na ₂ O·2MoO ₃ ..	82.28	82.28	Pale-yellow needles.
Na ₂ O·3MoO ₃ ..	87.39	87.48	Light-gray acicular crystals
Na ₂ O·4MoO ₃ ..	90.27	90.31	Gray prisms
Na ₂ O·5MoO ₃ ..	92.00	92.06	Gray prismatic crystals
K ₂ O·2MoO ₃ ..	75.35	75.36	Pale-yellow prisms
K ₂ O·3MoO ₃ ..	82.92	82.93	Light-gray needles
K ₂ O·4MoO ₃ ..	85.89	85.94	Gray prisms
K ₂ O·5MoO ₃ ..	88.40	88.43	Clusters of gray prisms
Rb ₂ O·2MoO ₃ ..	60.64	60.64	Prisms of uncertain shape
Rb ₂ O·3MoO ₃ ..	70.13	70.12	Light-gray needles
Rb ₂ O·4MoO ₃ ..	75.48	75.49	Gray prisms
Rb ₂ O·5MoO ₃ ..	79.28	79.28	Elongated gray prisms
Cs ₂ O·2MoO ₃ ..	50.62	50.62	Faintly manifested pale-yellow needles
Cs ₂ O·3MoO ₃ ..	60.51	60.51	Gray needles
Cs ₂ O·4MoO ₃ ..	66.33	66.36	Gray prisms
Cs ₂ O·5MoO ₃ ..	71.80	71.86	Elongated gray prisms

The experiments on the hydration of the isopolymolybdates were carried out as follows. A sample of the finely pulverized preparation was reacted with ten times its weight of water. The water treatment was performed in the cold, with periodic stirring, as well as in boiling water. In the former case the experiment lasted 24 hours, and 1 hour in the latter. Usually several runs were made at room temperature, followed by 1-3 runs in boiling water. After the treatment with water, the liquid was decanted from the insoluble residue, and a few milliliters of a 10% solution of ammonium nitrate were added to coagulate the turbidity. Then the transparent solution was transferred via a small siphon and evaporated in a platinum beaker. The dry residue was calcined and weighed, analysis indicated the composition of the fraction of the original alloy that entered solution. The coagulated suspension recovered in every run was added to the insoluble residue, dried at 120°, and analyzed.

For this investigation we prepared alloys of the following isopolymolybdates: Me₂O·2MoO₃, Me₂O·3MoO₃, Me₂O·4MoO₃ and Me₂O·5MoO₃, for all the alkali elements. The isopolymolybdates of lithium, sodium, potassium, and rubidium were prepared by fusing calculated quantities of molybdic anhydride with the respective carbonates, normal cesium molybdate being used for the cesium salts. The results of analysis and the external appearance of the resultant isopolymolybdate alloys are listed in Table 1. The initial alloys were analyzed gravimetrically, the molybdenum being determined as lead molybdate. The hydration product was analyzed volumetrically. A weighed amount of the molybdate to be analyzed of the order of 0.1 g, was placed in a 250-ml graduated flask and dissolved in 10 ml of 1N sodium hydroxide solution. Then 100 ml of distilled water was added, and 10 ml

of 2N sulfuric acid. To the solution thus acidulated there was added 5 g of granulated zinc or cadmium. The contents of the flask were cautiously heated to boiling and then evaporated to a volume of 30 ml. While the molybdenum was being reduced, the color was observed to change gradually from green to blue, dark-blue, crimson, and finally dark-brown. Five ml of an 8% solution of ammonium ferric alum was added to the chilled solution, together with some 75 ml of distilled water. The resultant transparent light-green liquid was decanted from the zinc into another flask and titrated with a 0.1 N permanganate solution. A blank test with pure molybdic anhydride was always run in parallel as a check, the amount of the anhydride used corresponding approximately to its percentage in the preparation under test. This method yields satisfactory results and is simpler than Somey's amalgam procedure.

EXPERIMENTAL

1. Lithium isopolymolybdates. The results of hydrating alloys of lithium isopolymolybdates are listed in Tables 2 and 3. As we see in Table 2, the percentage of the compounds that dissolves gradually diminishes as the water treatment of a weighed sample of an alloy progresses. Though, for example, the initial water-leaching of the $\text{Li}_2\text{O} \cdot 3\text{MoO}_3$ alloy in the cold dissolved 34.2% of the initial amount, the sixth such leaching dissolved less than 1%.

Processing alloys with the composition of $\text{Li}_2\text{O} \cdot 2\text{MoO}_3$ and $\text{Li}_2\text{O} \cdot 3\text{MoO}_3$ with cold water indicated that the first fraction of the soluble portion contained 90.1 - 90.2% MoO_3 , whereas lithium dimolybdate contains 90.59% MoO_3 . This is

TABLE 2

Composition of the Soluble Portion After Hydration of Alloys of
Lithium Acid Molybdates

Li ₂ O:MoO ₃ ratio in the initial alloy	% MoO ₃ in the alloy	Initial weight, grams	Treat- ment No.	Kind of treat- ment	Dissolved		MoO ₃ , %	Closest Compound
					Grams	% of initial weight		
1:2	90.61	2.0185	1	Cold	1.8988	94.07	90.11	Li ₂ Mo ₂ O ₇
			2	"	0.1093	5.41	94.00	Li ₂ Mo ₄ O ₁₃
			Total		2.0081	99.48	-	-
1:3	93.50	1.9705	1	Cold	0.6751	34.24	90.18	Li ₂ Mo ₂ O ₇
			2	"	0.2307	11.70	90.37	"
			3	"	0.1695	8.59	93.33	Li ₂ Mo ₃ O ₁₀
			4	"	0.1338	6.78	93.49	"
			5 - 6	"	0.1160	5.87	94.50	Li ₂ Mo ₄ O ₁₃
1:4	95.00	1.9801	Total		1.3251	67.18	-	-
			1	Cold	0.2575	13.00	90.61	Li ₂ Mo ₂ O ₇
			2	"	0.2133	10.77	91.35	"
			3	"	0.1776	8.93	92.03	Li ₂ Mo ₃ O ₁₀
			4	"	0.1396	7.05	93.10	"
			5	"	0.0729	3.65	94.66	Li ₂ Mo ₄ O ₁₃
1:5	95.85	3.9990	Total		0.8609	43.40	-	-
			1	Cold	0.6986	17.47	90.97	Li ₂ Mo ₂ O ₇
			2	"	0.4573	11.44	91.95	"
			3	"	0.3898	9.75	92.27	Li ₂ Mo ₃ O ₁₀
			4	"	0.3045	7.61	92.43	"
			5	"	0.2794	6.74	93.20	"
			6 - 7	"	0.4797	11.99	93.60	"
			8	Hot	0.5302	13.25	94.70	Li ₂ Mo ₄ O ₁₃
			Total		3.1395	78.25	-	-

TABLE 3

Composition of the Insoluble Residues After Hydration of Alloys of
Lithium Acid Molybdates

Li ₂ O:MoO ₃ ratio in the initial alloy	Per cent MoO ₃ in the alloy	Initial weight, grams	Insoluble residue		Per cent MoO ₃	Closest compound
			Grams	Per cent of initial weight		
1:2	90.61	2.0185	0.0087	0.43	Not de- termined	-
1:3	93.50	1.9705	0.6453	32.71	97.87	MoO ₃
1:4	95.00	1.9801	1.1189	56.57	99.05	"
1:5	95.85	3.9990	0.8328	20.83	99.98	"

unmistakable evidence that the lithium dimolybdate present decomposes partially, possibly even during its very crystallization, to form the normal molybdate and some more highly acid compound, say the tetramolybdate anhydride.

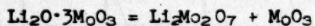
Lithium dimolybdate is likewise found in the alloys of the $\text{Li}_2\text{O} \cdot 4\text{M}_2\text{O}_3$ and $\text{Li}_2\text{O} \cdot 5\text{M}_2\text{O}_3$ type, as is shown by analysis of the initial fractions of their soluble portions. In the presence of a certain excess of molybdic anhydride the decomposition of the dimolybdate is apparently diminished, in accordance with the following equation or a similar one: $\text{Li}_2\text{Mo}_2\text{O}_7 \rightleftharpoons \text{Li}_2\text{MoO}_4 + \text{MoO}_3$. In particular the initial fraction of soluble matter secured in the hydration of the $\text{Li}_2\text{O} \cdot 4\text{M}_2\text{O}_3$ alloy has exactly the same composition as lithium dimolybdate. The analogous fraction secured after the water processing of the $\text{Li}_2\text{O} \cdot 5\text{M}_2\text{O}_3$ alloy is somewhat contaminated by more highly acid compounds (it contains 90.97% MoO_3 as against the 90.59% required for $\text{Li}_2\text{Mo}_2\text{O}_7$).

The fact that lithium dimolybdate is found in all the alloys investigated, from $\text{Li}_2\text{O} \cdot 2\text{M}_2\text{O}_3$ to $\text{Li}_2\text{O} \cdot 5\text{M}_2\text{O}_3$, enables us to assert on the basis of the phase rule - that at room temperature the $\text{Li}_2\text{MoO}_4 - \text{MoO}_3$ system can contain in addition to the dimolybdate, only one other compound, richer in molybdenum, which is common to all the alloys mentioned.

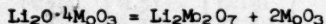
None of the tested alloys of lithium acid molybdates dissolves completely in water, all of them leaving more or less of an insoluble residue, depending upon their composition. The amount of the residue increases as the acidity of the compounds rises. Table 3 gives the composition and magnitude of the insoluble residues secured after processing various alloys of lithium acid molybdates with water.

The insoluble residues left behind after the water-processing of all the tested alloys of lithium acid molybdates consist essentially of molybdic anhydride, their MoO_3 content ranging from 97.97 to 99.98%. In the $\text{Li}_2\text{O} \cdot 2\text{M}_2\text{O}_3$ alloy the insoluble residue could not be analyzed owing to its smallness. Its qualitative properties indicated, however, that it, too, was molybdic anhydride.

The amount of insoluble residue obtained after hydrating $\text{Li}_2\text{O} \cdot 3\text{M}_2\text{O}_3$ and $\text{Li}_2\text{O} \cdot 4\text{M}_2\text{O}_3$ alloys is fairly close to the quantity corresponding to the presence of a mixture of lithium dimolybdate and molybdic anhydride in these alloys:



and



In the former case the alloy ought to contain 31.18% free molybdic anhydride (the insoluble residue totalled 32.71%). The theoretical percentage of free MoO_3 in the $\text{Li}_2\text{O} \cdot 4\text{M}_2\text{O}_3$ alloy is 47.54%, whereas the insoluble residue totalled 56.57%. These figures cannot be expected to coincide accurately, to be sure, since the insoluble residue will still contain traces of the dimolybdate if leaching is inadequate, while too intensive leaching will cause even the molybdic anhydride to dissolve perceptibly. This is the reason for the lowered yield of the insoluble residue in the test of the $\text{Li}_2\text{O} \cdot 5\text{M}_2\text{O}_3$ alloy, in which the final leaching operation was performed by boiling (the insoluble residue totalled 20.83%, whereas the alloy should contain 57.61% of free MoO_3 according to calculations). It should be added that the increased solubility of the molybdic anhydride may be caused by its reacting chemically with the hydrolysis products of the lithium dimolybdate (see below: experiments on hydrating sodium isopolymolybdates).

The average composition of the intermediate fractions obtained in processing the alloys of the lithium acid molybdates with water resembles that

of the trimolybdate in some instances and that of the tetramolybdate in others, though we can hardly say that these compounds are present in the initial alloys. It is more likely that when the product treated with water contains a high percentage of molybdic anhydride, more of the MoO_3 dissolves as indicated above, owing to its chemical interaction with the products of the hydrolysis of the lithium dimolybdate.

Hence, our investigation of alloys of lithium acid molybdates by the hydration method enables us to make the confident assertion that they contain only two compounds - lithium dimolybdate and free molybdic anhydride. Compounds such as lithium tri- and tetramolybdate, if formed during crystallization, are evidently decomposed completely during the cooling of the alloy.

2. Sodium isopolymolybdates. Processing alloys of sodium acid molybdates with water yielded results that resembled those described for the lithium isopolymolybdates. The respective experimental data are given in Tables 4 and 5. Leaching the soluble matter out of the $\text{Na}_2\text{O} \cdot 2\text{MoO}_3$ and $\text{Na}_2\text{O} \cdot 3\text{MoO}_3$ alloys with cold water indicated that the initial fractions contained 81.91 and 82.39% of molybdic anhydride, respectively. This is extremely close to the composition of sodium dimolybdate (containing 82.28% MoO_3 theoretically). Sodium dimolybdate was likewise found in the $\text{Na}_2\text{O} \cdot 4\text{MoO}_3$ and $\text{Na}_2\text{O} \cdot 5\text{MoO}_3$ alloys. Analyses of the initial fractions of these alloys indicated, however, a slightly higher MoO_3 content (83.27 and 83.39%), which must be attributed to the dissolution of the more highly acid compounds in the rather insoluble residue.

TABLE 4
Composition of the Soluble Portion After Hydration of Alloys
of Sodium Acid Molybdates

$\text{Na}_2\text{O}:\text{MoO}_3$ ratio in the ini- tial alloy	% MoO_3 in the alloy	Initial weight, grams	Treat- ment No.	Kind of treat- ment	Dissolved		MoO_3 , %	Closest compound
					Grams	% of initial weight		
1 : 2	82.28	3.9991	1	Cold	2.5495	63.75	81.91	$\text{Na}_2\text{Mo}_2\text{O}_7$
			2	"	1.0704	26.76	82.27	"
			3	"	0.3256	8.16	82.57	"
			4-5	"	0.0468	1.17	Not deter- mined	-
			Total.....		3.9923	99.84	-	-
1 : 3	87.39	4.0020	1	Cold	2.5176	62.91	82.39	$\text{Na}_2\text{Mo}_2\text{O}_7$
			2	"	1.1815	29.52	86.52	$\text{Na}_2\text{Mo}_3\text{O}_{10}$
			3	"	0.1486	3.73	90.63	$\text{Na}_2\text{Mo}_4\text{O}_{13}$
			4-5	"	0.0477	1.19	Not deter- mined	-
			Total.....		3.8954	97.35	-	-
1 : 4	90.27	4.0039	1	Cold	1.7262	43.19	83.27	$\text{Na}_2\text{Mo}_2\text{O}_7$
			2	"	1.0323	25.78	88.59	$\text{Na}_2\text{Mo}_3\text{O}_{10}$
			3	"	0.4508	11.26	90.13	$\text{Na}_2\text{Mo}_4\text{O}_{13}$
			4	"	0.2696	6.73	90.97	"
			5-6	"	0.1413	3.43	91.39	"
			Total.....		3.6202	90.39	-	-
1 : 5	92.00	4.0000	1	Cold	1.4857	37.16	83.93	$\text{Na}_2\text{Mo}_2\text{O}_7$
			2	"	0.8972	22.45	89.71	$\text{Na}_2\text{Mo}_3\text{O}_{10}$
			3	"	0.2367	5.92	90.97	$\text{Na}_2\text{Mo}_4\text{O}_{13}$
			4-5	"	0.1560	3.89	91.03	"
			6	Hot	0.2556	6.39	96.70	$\text{Na}_2\text{Mo}_4\text{O}_{13}$ + MoO_3
			Total.....		3.0212	75.81	-	-

TABLE 5

Composition of the Insoluble Residues After Hydration of Alloys
of Sodium Acid Molybdates

Na ₂ :MoO ₃ ratio in the initial alloy	Per cent MoO ₃ in the alloy	Initial weight, grams	Insoluble residue		Per cent MoO ₃	Closest Compound
			Grams	Per cent of initial weight		
1 : 2	82.28	3.9991	0.0036	0.09	Not deter- mined	-
1 : 3	87.39	4.0020	0.1052	2.63	99.99	MoO ₃
1 : 4	90.27	4.0039	0.3637	9.02	99.47	"
1 : 5	92.00	4.0000	0.9560	23.90	99.99	"

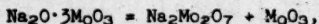
The presence of sodium dimolybdate in all the alloys tested, even in the most highly acid ones, forces us to conclude that if a more highly acid compound is present in the systems tested, it must be identical in all the alloys.

Pure sodium dimolybdate apparently fuses with some decomposition as follows: $\text{Na}_2\text{Mo}_2\text{O}_7 \rightarrow \text{Na}_2\text{MoO}_4 + \text{MoO}_3$. This is evidenced by the fact that the percentage of molybdic anhydride in the initial lixiviation fraction of the Na₂O·2MoO₃ alloy is perceptibly below the theoretical figure. The decomposition of the dimolybdate diminishes in the more highly acid alloys, the composition of the 1st leaching fraction of the Na₂O·3MoO₃ alloy being exactly the same as that of the dimolybdate.

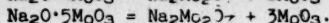
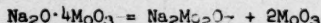
Table 4 shows that the insoluble residue left after the Na₂O·3MoO₃, Na₂O·4MoO₃, and Na₂O·5MoO₃ alloys are hydrated consists of pure molybdic anhydride (containing 99.47 - 99.99% MoO₃). We were unable to analyze the insoluble residue of the Na₂O·2MoO₃ alloy owing to the minute quantity available, but qualitative tests indicated that it was molybdenum trioxide as well.

Thus, the only compound we can expect to find in alloys of sodium acid molybdates is Na₂Mo₂O₇. Even if sodium tri- or tetramolybdate is formed during solidification of the melt in question, these compounds evidently break down during subsequent cooling. The size of the insoluble residue increases with the percentage of molybdic anhydride in the alloys. It is worthy of note, however, that alloys of sodium acid molybdates whose molecular composition resembles that of lithium molybdates always yield less insoluble residue. For the Na₂O·3MoO₃ alloy, for example, the insoluble residue was 2.63% of the initial weight, whereas the insoluble residue of the corresponding lithium alloy is 12 times as great. This must apparently be attributed to the fact that the hydration products of the alloys of sodium acid molybdates react with the insoluble residue to a greater extent. And, in accordance with this principle, a second processing of the Na₂O·3MoO₃ alloy with water causes about 30% of the initial weight to enter solution, its average composition approaching that of Na₂Mo₂O₇.

On the assumption that the only constituents present in solidified alloys of sodium acid molybdates are Na₂Mo₂O₇ and MoO₃, we can represent these alloys as mixtures of the following composition:



and



In this case the $\text{Na}_2\text{O} \cdot 3\text{MoO}_3$ alloy ought to contain 29.15% of free molybdc anhydride (the insoluble residue was found to be 2.63%). The theoretical content of free MoO_3 in the $\text{Na}_2\text{O} \cdot 4\text{MoO}_3$ and $\text{Na}_2\text{O} \cdot 5\text{MoO}_3$ alloys should equal 45.14 and 55.24%, respectively (the insoluble residues were found to total 9.02 and 23.90%, respectively). The following considerations must be borne in mind in any attempt to explain these singularities in the behavior of sodium acid molybdates. E.F.Krauze and A.V.Novoselova [7] found that the solubility of molybdc anhydride in water at room temperature was 0.8 gram/liter. Our experiments on the processing of molybdc anhydride with water under the conditions ordinarily employed for hydration have shown that 100ml of water dissolves 0.06 g MoO_3 in the cold in 24 hours. When the processing is effected with a solution that contains 0.2 g of sodium dimolybdate in 100ml of water, the solubility of the molybdc anhydride is increased by a factor of 2.1. Thus, there is no doubt that aqueous sodium molybdates react with molybdc anhydride.

3. Potassium isopolymolybdates. Lixiviation of alloys of potassium acid molybdates with water yields results that diverge markedly from those secured in water-processing of the respective preparations of lithium and sodium (see Tables 6 and 7).

TABLE 6

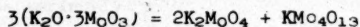
Composition of the Soluble Portion After Hydration of Alloys of Potassium Acid Molybdates

$\text{K}_2\text{O}:\text{MoO}_3$ ratio in the initial alloy	% MoO_3 in the alloy	Initial weight, grams	Treat- ment No.	Kind of treat- ment	Dissolved		MoO_3 , %	Closest compound
					Grams	% of initial weight		
1 : 2	75.35	3.9993	1	Cold	1.0954	27.39	61.57	K_2MoO_4
			2	"	0.2005	5.01	63.94	"
			3	"	0.1209	3.02	65.87	"
			4 - 6	"	0.1772	4.43	83.19	$\text{K}_2\text{Mo}_3\text{O}_{10}$
			7	Hot	0.0620	1.55	Not deter- mined.	-
			Total		1.6560	41.40	-	-
1 : 3	82.92	4.0015	1	Cold	0.4585	11.46	62.90	K_2MoO_4
			2	"	0.1293	3.23	81.34	$\text{K}_2\text{Mo}_3\text{O}_{10}$
			3 - 4	"	0.1758	4.40	82.17	"
			5 - 6	"	0.1247	3.12	82.57	"
			7	Hot	0.0555	1.39	Not deter- mined.	-
			Total		0.9438	23.60	-	-
1 : 4	85.89	4.0008	1	Cold	0.1036	2.59	19.14	$\text{K}_2\text{Mo}_3\text{O}_{10}$
			2 - 6	"	0.1374	3.42	81.08	"
			7	Hot	0.3198	7.99	85.28	$\text{K}_2\text{Mo}_4\text{O}_{13}$
			8	"	0.3025	7.56	85.59	"
			Total		0.8633	21.56	-	-
1 : 5	88.40	4.0016	1	Cold	0.1347	3.37	80.89	$\text{K}_2\text{Mo}_3\text{O}_{10}$
			2	"	0.1042	2.60	81.43	"
			3 - 4	"	0.1654	4.13	82.23	"
			5 - 6	"	0.1410	3.51	83.12	"
			7	Hot	0.5140	12.85	85.43	$\text{K}_2\text{Mo}_4\text{O}_{13}$
			8	"	0.4465	11.16	85.55	"
			Total		1.5058	37.62	-	-

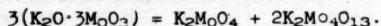
The action of cold water upon the $K_2O \cdot 2MoO_3$ and $K_2O \cdot 3MoO_3$ alloys indicated that the molybdc anhydride constituted only 61.57 and 62.90%, respectively of the initial fraction of the soluble portion, which is the figure for normal potassium molybdate (K_2MoO_4 contains 60.40% MoO_3). A more acid molybdate apparently also dissolves alongside the normal molybdate to some extent. As a result, even the initial fractions resulting from the aqueous lixiviation of alloys of potassium acid molybdates have a somewhat higher percentage of molybdc anhydride than is called for by K_2MoO_4 . There is no doubt that the normal potassium molybdate is likewise present in alloys of the $K_2O \cdot 4MoO_3$ and $K_2O \cdot 5MoO_3$ type, as may be seen from the qualitative observations made on the initial fractions of their soluble portion. These fractions, after having dried and fused for analysis, were white in color and perceptibly hygroscopic (a property of normal potassium molybdate). These fractions had a high percentage of molybdc anhydride (79.14 and 80.89% respectively), approaching that of the compound $K_2Mo_3O_{10}$, on the average. It should be noted that the volume of the initial fractions resulting from the cold-water treatment drops considerably as the percentage of MoO_3 in the tested preparations rises (Table 6). The total soluble portion drops particularly sharply in the case of the alloy $K_2O \cdot 4MoO_3$, the drop remaining essentially the same in the alloy $K_2O \cdot 5MoO_3$. As Table 7 shows, the insoluble residue left after the processing of all the tested alloys of potassium acid molybdates with water is mainly the potassium tetramolybdate, $K_2Mo_4O_{13}$, corresponding to the theoretical content of 85.96% MoO_3 . The insoluble residues of the alloys $K_2O \cdot 2MoO_3$ and $K_2O \cdot 3MoO_3$ contained 86.02 and 86.10% of molybdc anhydride, respectively. When fused for analysis, it consisted of gray crystals that resembled the prisms of potassium tetramolybdate recovered from the respective melts.

The $K_2O \cdot 4MoO_3$ and $K_2O \cdot 5MoO_3$ alloys exhibited a higher percentage of molybdc anhydride in the insoluble residue, to wit, 87.41 and 87.67% of MoO_3 , respectively, figures that lie between those for $K_2Mo_4O_{13}$ and $K_2Mo_5O_{16}$.

The amount of insoluble residue secured after hydration of the alloys with a composition of $K_2O \cdot 2MoO_3$ and $K_2O \cdot 3MoO_3$ was fairly close to what would correspond to the presence of a mixture of potassium normal molybdate and tetramolybdate, viz:



and



In the former case the alloy ought to contain 58.45% of potassium tetramolybdate (the insoluble residue was found to be 58.49%). The theoretical percentage of the tetramolybdate in the $K_2O \cdot 3MoO_3$ alloy is 84.91% (the insoluble residue was found to be 75.89%).

These experimental data seem to indicate that under the conditions of our tests normal potassium molybdate dissolves in cold water completely, while the tetramolybdate dissolves but slightly. The tetramolybdate dissolves appreciably in boiling water, however, as may be seen in hydration experiments Numbers 7 and 8 with the $K_2O \cdot 4MoO_3$ alloy (Table 6). The dissolved product contained 85.28 — 85.59% of molybdc anhydride. In analogous tests of the alloy $K_2O \cdot 5MoO_3$, the hot-hydration fraction contained 85.43 — 85.55% MoO_3 ($K_2Mo_4O_{13}$ contains 85.96% MoO_3).

When we compare the last fractions of the cold-hydration tests with tests in which hot-water processing was used, we note that raising the temperature increases the quantity of material dissolved out the $K_2O \cdot 2MoO_3$ and $K_2O \cdot 3MoO_3$ alloys only slightly. A similar shift from cold-water to hot-water

hydration of the alloys $K_2O \cdot 4MoO_3$ and $K_2O \cdot 5MoO_3$ results in a much greater increase in the weight of the dissolving fractions (by a factor of 8 to 15). It may be that this is affected by the differing size of the alloy crystals.

TABLE 7

Composition of the Insoluble Residues After Hydration of Alloys of Potassium Acid Molybdates

K ₂ O · MoO ₃ ratio in the initial alloy	Per cent MoO ₃ in the alloy	Initial weight, grams	Insoluble residue		Per cent MoO ₃	Closest compound
			Grams	Per cent of initial weight		
1 : 2	75.35	3.9993	2.3593	58.49	86.02	K ₂ Mo ₄ O ₁₀
1 : 3	82.92	4.0015	3.0367	75.89	86.10	"
1 : 4	85.89	4.0008	3.1140	77.84	87.41	K ₂ Mo ₄ O ₁₀ + MoO ₃
1 : 5	88.40	4.0016	2.4757	61.87	87.67	"

No special study was made of the nature of the process involved in the dissolution of potassium tetramolybdate. There is no doubt, however, that this is a complex process and largely involves a transition to potassium aquopolymolybdates. Potassium tetramolybdate apparently is partially decomposed at the temperature at which it separates out from the melt. Inasmuch as no dimolybdate was found in the $K_2O \cdot 2MoO_3$ alloy, while potassium trimolybdate was found in the $K_2O \cdot 3MoO_3$ alloy, it must be assumed that the tetramolybdate decomposes as follows: $K_2Mo_4O_{10} \rightleftharpoons K_2MoO_4 + 3MoO_3$.

The normal potassium molybdate is a constituent of the $K_2O \cdot 2MoO_3$ and $K_2O \cdot 3MoO_3$ alloys, separating out of the melt in equilibrium with the tetramolybdate. Here again the percentage of the K_2MoO_4 in the alloy is much higher. In the alloys with the composition of $K_2O \cdot 4MoO_3$ and $K_2O \cdot 5MoO_3$, however, the normal potassium molybdate is present only as a product of the partial decomposition of the tetramolybdate, decomposing during the water processing and contaminating the tetramolybdate seriously.

The average composition of the intermediate fractions secured in the water-processing of alloys of potassium acid molybdates (such as Fractions 4-6 of the $K_2O \cdot 2MoO_3$ and Fractions 2-7 of the $K_2O \cdot MoO_3$ alloys) resembles that of potassium trimolybdate. Everything that has been set forth above, however, forces us to assume that they are mixtures of normal potassium molybdate and the tetramolybdate, a small quantity of which (say, some two per cent of the initial weight) may enter solution under our experimental conditions.

Thus, investigation of alloys of potassium acid molybdates by the method of fractional lixiviation with water indicates that they contain only one isopolymolybdate — $K_2Mo_4O_{10}$. The $K_2O \cdot 2MoO_3$ and $K_2O \cdot 3MoO_3$ alloys contain the normal molybdate in addition to the tetramolybdate, while the $K_2O \cdot 4MoO_3$ alloy consists chiefly of potassium tetramolybdate with traces of K_2MoO_4 and MoO_3 due to the partial decomposition of the tetramolybdate. In the more highly acid alloy, $K_2O \cdot 5MoO_3$, it would seem that no new isopolymolybdates are formed, the alloy containing the tetramolybdate mixed with free molybdic anhydride and a trace of the normal molybdate.

4. Isopolymolybdates of rubidium and cesium. The data on the action of water upon alloys of the acid molybdates of rubidium and cesium are listed in Tables 8, 9, 10, and 11. These results are similar and remind one of those described above for the potassium preparations. When the alloys $\text{Rb}_2\text{O} \cdot 2\text{MoO}_3$ and $\text{Cs}_2\text{O} \cdot 2\text{MoO}_3$ were treated with water, the initial fractions of the soluble portion contained 43.65 and 34.06% of molybdic anhydride respectively. Under analogous conditions, compounds with a somewhat higher content of molybdenum trioxide (46.03 and 37.36% MoO_3 , respectively) entered solution from the $\text{Rb}_2\text{O} \cdot 3\text{MoO}_3$ and $\text{Cs}_2\text{O} \cdot 3\text{MoO}_3$ alloys. The composition of the foregoing fractions is closest to that of the normal molybdates of rubidium and cesium (Rb_2MoO_4 contains 41.54% MoO_3 , while Cs_2MoO_4 contains 33.82% MoO_3). In addition to the normal molybdates, these alloys also contain more highly acid compounds, hydration of these latter causing the soluble fractions to display a higher content of molybdic anhydride than the percentage required for normal molybdates (Tables 8 and 9).

TABLE 8

Composition of the Soluble Portion After Hydration of Alloys of Rubidium Acid Molybdates

$\text{Rb}_2\text{O} \cdot \text{MoO}_3$ ratio in the initial alloy	% MoO_3 in the alloy	Initial weight, grams	Treatment No.	Kind of treatment	Dissolved		MoO_3 , %	Closest compound
					Grams	% of initial weight		
1 : 2	60.64	4.0012	1	cold	1.1450	28.62	43.65	Rb_2MoO_4
			2	"	0.9483	23.69	52.57	$\text{Rb}_2\text{Mo}_2\text{O}_7$
			3	"	0.8565	21.40	53.03	"
			4	"	0.5643	14.43	53.87	"
			5	"	0.1385	3.45	53.92	"
			Total.....		3.6526	91.59	—	—
1 : 3	70.13	3.9995	1	cold	0.2457	6.14	41.03	Rb_2MoO_4
			2	"	0.1319	3.30	65.94	$\text{Rb}_2\text{Mo}_3\text{O}_{10}$
			3	"	0.1113	2.78	66.77	"
			4 and 5	"	0.2110	5.27	67.83	"
			6	hot	0.5261	13.15	73.45	$\text{Rb}_2\text{Mo}_4\text{O}_{13}$
			7 - 9	"	0.2342	5.85	75.02	"
1 : 4	75.48	4.0001	Total.....		1.4602	36.49	—	—
			1	cold	0.0813	2.02	72.32	$\text{Rb}_2\text{Mo}_3\text{O}_{10}$
			2 - 5	"	0.0833	2.09	74.86	$\text{Rb}_2\text{Mo}_4\text{O}_{13}$
			6	hot	0.1208	3.02	75.02	"
			7 - 9	"	0.1993	4.95	75.21	"
			Total.....		0.4847	12.08	—	—
1 : 5	79.28	4.0000	1	cold	0.0974	2.43	73.19	$\text{Rb}_2\text{Mo}_2\text{O}_{10}$
			2 - 5	"	0.1070	2.67	75.02	$\text{Rb}_2\text{Mo}_4\text{O}_{13}$
			6	hot	0.1295	3.23	75.61	"
			7 - 9	"	0.3104	7.75	75.73	"
			Total.....		0.6543	16.08	—	—

It is likely that the normal molybdates of rubidium and cesium are also present in the alloys of the $\text{Me}_2\text{O} \cdot 4\text{MoO}_3$ and $\text{Me}_2\text{O} \cdot 5\text{MoO}_3$ type. Qualitative observations indicate that the initial fractions of the soluble portion of these alloys possess, after drying and calcination, some of the properties of the normal molybdates of rubidium and cesium, such as their hygroscopicity. The

percentage of molybdic anhydride in these products was perceptibly higher, however, than the figure required for normal molybdates, being closer to the trimolybdates. We see in Tables 10 and 11 that the insoluble portion left after all these alloys of the acid molybdates of rubidium and cesium had been processed with water had a composition resembling that of the tetramolybdates.

TABLE 9

Composition of the Soluble Portion After Hydration of Alloys of Cesium Acid Molybdates.

Cs ₂ O:MoO ₃ ratio in the initial alloy	MoO ₃ in the alloy	Initial weight, grams	Treat- ment No.	Kind of treat- ment	Dissolved		MoO ₃ , %	Closest compound
					Grams	% of initial weight		
1 : 2	50.62	2.0013	1	cold	0.6469	32.32	34.06	Cs ₂ MoO ₄
			2	"	0.3067	15.33	43.27	Cs ₂ Mo ₂ O ₇
			3,4,5	"	0.1833	9.15	45.08	"
			6	hot	0.2655	13.27	59.35	Cs ₂ Mo ₃ O ₁₀
			7,8,9	"	0.2588	13.44	61.11	"
			Total.....		1.6612	83.51	—	—
1 : 3	60.51	2.0010	1	cold	0.2240	11.19	37.36	Cs ₂ MoO ₄
			2	"	0.0905	4.52	45.76	Cs ₂ Mo ₂ O ₇
			3,4,5	"	0.2530	12.63	61.19	Cs ₂ Mo ₃ O ₁₀
			6	hot	0.3382	16.19	64.89	Cs ₂ Mo ₄ O ₁₃
			7,8,9	"	0.3659	18.29	65.12	"
			Total.....		1.2716	62.82	—	—
1 : 4	66.33	2.0033	1	cold	0.1485	7.39	58.70	Cs ₂ Mo ₃ O ₁₀
			2,3,	"	0.1763	8.80	65.85	Cs ₂ Mo ₄ O ₁₃
			4,5	"				
			6,7,	hot	0.1409	7.03	66.04	"
			8,9					
			Total.....		0.4657	23.22	—	—
1 : 5	71.80	2.0022	1	cold	0.0739	3.69	59.85	Cs ₂ Mo ₃ O ₁₀
			2,3,	"	0.0371	1.84	66.05	Cs ₂ Mo ₄ O ₁₃
			4,5					
			6,7,	hot	0.1477	7.35	66.36	"
			8,9					
			Total.....		0.2587	12.88	—	—

The residue left after hydration of alloys of the Me₂O·2MoO₃ and Me₂O·3MoO₃ types contained 75.05 and 76.63% respectively, of MoO₃ in the rubidium preparations and 65.42 and 66.83% respectively, in the cesium preparations (the theoretical content of molybdic anhydride is 75.49% in Rb₂Mo₄O₁₃ and 66.36% in Cs₂Mo₄O₁₃). In the alloys of the Me₂O·4MoO₃ and Me₂O·5MoO₃ types, the insoluble portions exhibited a somewhat higher percentage of molybdenum trioxide, namely : 76.07 and 77.18% MoO₃, respectively, in the rubidium preparations and 67.30 and 71.94% MoO₃, respectively, in the cesium preparations. The residues after hydration of the Rb₂O·2MoO₃ and Cs₂O·4MoO₃ alloys consisted, after they had been dried and calcined, of gray prism, the form of which resembled that of the crystals of potassium tetramolybdate. The percentage of molybdic anhydride in the insoluble hydration residues of the alloys Rb₂O·4MoO₃, Rb₂O·5MoO₃, Cs₂O·4MoO₃, and Cs₂O·5MoO₃

TABLE 10

Composition of the Insoluble Residues After Hydration of Alloys of Rubidium Acid Molybdates

Rb ₂ MoO ₃ ratio in the initial alloy	% MoO ₃ in the alloy	Initial weight, grams	Insoluble residue		% MoO ₃	Closest compound
			Grams	% of initial weight		
1 : 2	60.64	4.0012	0.3328	8.32	75.05	Rb ₂ Mo ₄ O ₁₃
1 : 3	70.13	3.9995	2.5124	62.81	76.63	Rb ₂ Mo ₄ O ₁₃ + MoO ₃
1 : 4	75.48	4.0001	3.5034	87.58	76.07	"
1 : 5	79.28	4.0000	3.3438	83.60	77.18	"

TABLE 11

Composition of the Insoluble Residues after Hydration of Alloys of Cesium Acid Molybdates

Cs ₂ MoO ₃ ratio in the initial alloy	% MoO ₃ in the alloy	Initial weight, grams	Insoluble residue		% MoO ₃	Closest compound
			Grams	% of initial weight		
1 : 2	50.62	2.0013	0.3065	15.32	65.42	Cs ₂ Mo ₄ O ₁₃
1 : 3	60.51	2.0010	0.7124	36.05	66.83	"
1 : 4	66.33	2.0033	1.5192	75.83	67.30	Cs ₂ Mo ₄ O ₁₃ +MoO ₃
1 : 5	71.80	2.0022	1.7223	86.02	71.94	"

somewhat exceeded the content required for the tetramolybdates, but in the case of rubidium it did not attain the figure corresponding to the composition of the pentamolybdate.

Thus, as was the case in our investigation of the potassium molybdates, the tested alloys of the acid molybdates of rubidium and cesium of the Me₂O·2MoO₃ and Me₂O·3MoO₃ types consisted of mixtures of the normal molybdates and the tetramolybdates. The more highly acid alloys - with a composition of Me₂O·4MoO₃ - are distinguished by partial decomposition of the tetramolybdate they contain, as follows: Me₂Mo₄O₁₃ → Me₂MoO₄ + 3MoO₃. That is why these alloys contain molybdic anhydride and the corresponding normal molybdates in addition to the tetramolybdates. There is less of the normal molybdates present, however, than in the preparations with the composition of Me₂O·2MoO₃ and Me₂O·3MoO₃. Lastly, the alloys of the Me₂O·5MoO₃ type contain a high percentage of the free molybdic anhydride, with merely a trace of the normal molybdates.

The size of the insoluble residue recovered after hydration of the Rb₂O·2MoO₃ and Cs₂O·2MoO₃ alloys is much different from what we might expect on the assumption that these alloys are mixtures of the normal molybdate and the tetramolybdate: 3(Me₂O·2MoO₃) = 2Me₂MoO₄ + Me₂Mo₄O₁₃.

The insoluble residue of the Rb₂O·2MoO₃ totaled 8.32%, whereas it should have been 53.54% according to the foregoing equation. The Cs₂O·2MoO₃ alloy yielded 15.32% of an insoluble residue as against the calculated 50.27% of cesium tetramolybdate.

These discrepancies are readily understood, once we allow for the solubility of the tetramolybdates of rubidium and cesium as well as for the marked tendency of the normal molybdates of rubidium and cesium to react chemically with molybdic anhydride and the tetramolybdate in the insoluble residue. Analogous results were secured with the alloys of the $\text{Me}_2\text{O} \cdot 3\text{MoO}_3$ type.

As was the case with the potassium molybdates, no sign of the presence of di- or trimolybdates was found in our tests of the hydration of alloys of the acid molybdates of rubidium and cesium of the $\text{Me}_2\text{O} \cdot 2\text{MoO}_3$ and $\text{Me}_2\text{O} \cdot 3\text{MoO}_3$ type. The intermediate fractions secured in the lixiviation of these alloys, which have an average composition corresponding to that of di- or trimolybdates, must be regarded as mixtures containing the normal molybdate and the tetramolybdate. In the tested rubidium and cesium alloys no other isopoly compounds than the tetramolybdates appear to be formed. This is indicated by the fact that when even the most highly acid alloys ($\text{Me}_2\text{O} \cdot 4\text{MoO}_3$ and $\text{Me}_2\text{O} \cdot 5\text{MoO}_3$) are hydrated with cold water, they yield fractions whose average molybdic anhydride content is less than is required for the tetramolybdate. In still more highly acid compounds, such as the pentamolybdate, the composition of the alloy would be equivalent to mixtures of $\text{Me}_2\text{Mo}_4\text{O}_{13}$ and $\text{Me}_2\text{Mo}_5\text{O}_{16}$.

It would be impossible for the normal molybdate to be present in these instances, only the stated acid molybdates dissolving during hydration - which is contradicted by the experimental evidence. Hence, it must be supposed that in the acid alloys of rubidium and cesium molybdates the appearance of the tetramolybdates is directly followed by that of the molybdic anhydride.

It may be inferred from the experiments described that at room temperature lithium and sodium form only dimolybdates, of all the possible isopolymolybdates whereas potassium, rubidium, and cesium form only tetramolybdates. Hence, most of the compounds separating out from melts of the acid molybdates at high temperature and detected by thermal analysis decompose during the course of cooling. It should also be noted that the tendency toward the formation of stable isopoly compounds with a higher content of the acid anhydride in the anion increases with the radius of the cation of the alkali element. The lower the polarizing effect of the cation, the more complex the isopolymolybdate anion that may be attached to it ($\text{Mo}_4\text{O}_{13}^{2-}$ for ions of potassium, rubidium, and cesium, and $\text{Mo}_2\text{O}_7^{2-}$ for ions of lithium and sodium).

The alloys of lithium and sodium molybdates that are more highly acid than $\text{Me}_2\text{O} \cdot 2\text{MoO}_3$ contain free molybdic anhydride. The same holds true of the alloys of the molybdates of potassium, rubidium and cesium that are more highly acid than $\text{Me}_2\text{O} \cdot 4\text{MoO}_3$. It should also be borne in mind that the dimolybdates of lithium and sodium are apparently somewhat decomposed into molybdic anhydride and the normal molybdate during the very process of their separation from the melts. As the percentage of molybdic anhydride in the alloy rises, say up to the proportion of $\text{Me}_2\text{O} \cdot 3\text{MoO}_3$, this phenomenon becomes practically imperceptible. The decomposition of the tetramolybdates of potassium, rubidium, and cesium into molybdic anhydride and the normal molybdate is more pronounced, being perceptible even in $\text{Me}_2\text{O} \cdot 5\text{MoO}_3$ alloys. Table 12 shows what components are contained in alloys of various acid molybdates, depending on their composition. The compounds that are present merely as traces, due to the decomposition of the di- or tetramolybdates are indicated in parenthesis.

This research enables us to specify the conditions governing the production of the various isopolymolybdates. To prepare the dimolybdates of lithium or sodium it is advisable to use alloys in which the $\text{Me}_2\text{O}:\text{MoO}_3$ ratio is 1:1.8 or 1:1.9.

After the traces of the normal molybdate have been washed out of the alloy with cold water, the residue will consist of the dimolybdate. Preparation of the pure tetramolybdates of potassium, rubidium, or cesium requires the use of alloys having the composition of $\text{Me}_2\text{O} \cdot 3\text{MoO}_3$ or $\text{Me}_2\text{O} \cdot 5\text{MoO}_3$. The alloy is lixiviated several times in boiling water, the insoluble residue being the tetramolybdate.

TABLE 12

Composition of Alloys of Acid Molybdates of the Alkali Elements at Room temperature.

$\text{Me}_2\text{O}:\text{MoO}_3$ ratio in the alloy	Compounds present in the alloys	
	Lithium and sodium molybdates	Potassium, rubidium, and cesium molybdates
1:2	$\text{Me}_2\text{Mo}_2\text{O}_7(\text{Me}_2\text{MoO}_4, \text{MoO}_3)$	$\text{Me}_2\text{MoO}_4, \text{Me}_2\text{Mo}_4\text{O}_{13}$
1:3	$\text{Me}_2\text{Mo}_2\text{O}_7, \text{MoO}_3$	ditto
1:4	ditto	$\text{Me}_2\text{Mo}_4\text{O}_{13}(\text{Me}_2\text{MoO}_4, \text{MoO}_3)$
1:5	"	$\text{Me}_2\text{Mo}_4\text{O}_{13}, \text{MoO}_3(\text{Me}_2\text{MoO}_4)$

SUMMARY

1. The action of water upon alloys of the acid molybdates of the alkali elements, with compositions ranging from $\text{Me}_2\text{O} \cdot 2\text{MoO}_3$ to $\text{Me}_2\text{O} \cdot 5\text{MoO}_3$, has been investigated with the objective of determining the compounds they contain.
2. It has been found that at room temperature there is only one comparatively stable isopolymolybdate present for each alkali element. Lithium and sodium form dimolybdates, while potassium, rubidium, and cesium form tetramolybdates. The isopolymolybdates of different composition that separate out during the solidification of the molten salts are evidently decomposed during cooling.
3. The dimolybdates of lithium and sodium, and the tetramolybdates of potassium, rubidium, and cesium, are decomposed to some degree during fusion, giving rise to the normal molybdate and molybdic anhydride.
4. Isopolymolybdate alloys that are more highly acid than $\text{Li}_2\text{O} \cdot 2\text{MoO}_3$, $\text{Na}_2\text{O} \cdot 2\text{MoO}_3$, $\text{K}_2\text{O} \cdot 4\text{MoO}_3$, $\text{Rb}_2\text{O} \cdot 4\text{MoO}_3$ and $\text{Cs}_2\text{O} \cdot 4\text{MoO}_3$ contain a high percentage of free molybdic anhydride.
5. The dimolybdates of lithium and sodium are readily hydrated by cold water, being converted into soluble molybdates. The tetramolybdates of potassium, rubidium, and cesium are slowly hydrated in the cold and more rapidly in boiling water, likewise being converted into soluble compounds. Normal alkaline molybdates are most readily hydrated.
6. The most convenient procedure for isolating the dimolybdates of lithium and sodium and the tetramolybdates of potassium, rubidium, and cesium by the hydration method is outlined.

LITERATURE CITED

- [1] F. Hoermann, Z. Anorg. Ch., 177, 145 (1929).
- [2] E. Groschuff, Z. Anorg. Ch., 58, 113 (1908).
- [3] M. Amadori, Atti. Veneto, 72, II, 896 (1912-1913).
- [4] Vikt. I. Spitsyn and I. M. Kuleshov, J. Gen. Chem. 21, 1365 (1951). ¹⁾
- [5] L. Svanberg, H. Struve, J. pr. Ch., 44, 257 (1848).
- [6] Vikt. I. Spitsyn, J. Gen. Chem. 8, 869 (1938).
- [7] E. F. Krauze and A. V. Novoselova, Jour. Russ. Phys. Chem. Soc. 62, 287 (1930).

Received October 2, 1949.

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¹⁾ See C. B. English translation, p. 1493.

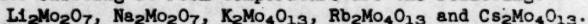
RESEARCH ON THE THERMAL STABILITY AND VOLATILITY OF THE
ISOPOLYMOLYBDATES OF THE ALKALI ELEMENTS

Vikt. I. Spitsyn and I.M. Kuleshov

In a previous paper [1] we have shown that potassium, rubidium, and cesium form considerable quantities of isopolymolybdates, which separate out when the respective melts solidify. Several isopolymolybdates are also described in the literature for lithium and sodium.

Investigation of alloys of the isopolymolybdates by the hydration method [2] has led us to conclude, however, that the number of compounds present in the alloys that have solidified and cooled to room temperature is much lower than that detected during the crystallization of the melts. It seems that chemical transformations occur below the solidus line in systems containing acid molybdates, involving the breakdown of some of the initially crystallized molybdates and the splitting out of molybdic anhydride or the formation of other, stabler isopolymolybdates.

This investigation established that the only isopolymolybdates of the alkali elements existing at room temperature are the following:



We were interested in determining whether these compounds are, in general, the most stable of the acid molybdates of each alkali element or are replaced by other types of compounds at higher temperatures.

The literature contains no mention of the thermal stability of isopolymolybdates. We have made a study of this stability under the conditions prevailing in investigations of the thermal stability and volatility of the normal molybdates of the alkali elements.

The initial isopolymolybdates were prepared by fusing a calculated quantity of molybdic anhydride with the respective carbonates (or with the normal molybdate in the case of cesium). The resultant preparations were analyzed by the plumbate method. The appearance of the isopolymolybdate alloys and a summary of the results of their analysis are given in our preceding paper [2].

We began with a study of the behavior of alloys with a composition equivalent to that of dimolybdates when calcined at 1200° (Table 1.) The preparations lose considerable weight at this temperature, the calcination residue exhibiting a lower percentage of molybdic anhydride than the initial salt. The highest loss of molybdenum trioxide was manifested by the lithium molybdate (61.42% of the initial content), with the sodium salt displaying the minimum loss (22.97%). The loss of molybdic anhydride is progressively higher in the molybdates of potassium, rubidium, and cesium, the loss of MoO_3 during the test being 53.21% for the latter salt.

The loss of weight of alloys with the composition of $\text{Me}_2\text{O} \cdot 2\text{MoO}_3$ is quite appreciable at 1200°. We therefore continued our investigation of the thermal stability of the isopolymolybdates of the alkali elements at a temperature of 1000°.

We see in Table 2 that at this temperature the loss of molybdic anhydride from alloys with the composition of $\text{Me}_2\text{O} \cdot 2\text{MoO}_3$ follows the same pattern as at 1200°. The maximum loss of molybdenum trioxide is exhibited by the lithium preparation (16.65%), with the minimum exhibited by sodium dimolybdate (4.14%).

Moreover, the loss of MoO_3 rises progressively as we pass to the alloys containing the molybdates of potassium, rubidium, and cesium (7.74, 9.15 and 11.30% respectively).

Table 3 gives the results of calcining alloys with a composition of $\text{Me}_2\text{O} \cdot 3\text{MoO}_3$ at 1000° .

TABLE 1

Calcination of $\text{Me}_2\text{O} \cdot 2\text{MoO}_3$ Alloys at 1200° . Calcination time: 6 hours.

Composition of preparation	Test No.	Weight, grams	Loss of weight		Percentage of MoO_3		Loss of MoO_3	
			Grams	Per cent	Before test	After test	Per cent of initial content	Mean value
$\text{Li}_2\text{O} \cdot 2\text{MoO}_3$	1	0.2017	0.1234	61.18	90.61	88.51	62.09	61.42
	2	0.1985	0.1188	59.87	90.61	88.58	60.75	
$\text{Na}_2\text{O} \cdot 2\text{MoO}_3$	3	0.2102	0.0485	23.08	82.28	81.82	23.53	22.97
	4	0.1991	0.0438	22.00	82.28	81.86	22.41	
$\text{K}_2\text{O} \cdot 2\text{MoO}_3$	5	0.2026	0.0612	30.23	75.35	74.40	31.11	30.74
	6	0.1973	0.0583	29.56	75.35	74.45	30.38	
$\text{Rb}_2\text{O} \cdot 2\text{MoO}_3$	7	0.2002	0.0962	48.06	60.64	58.56	49.84	49.24
	8	0.2335	0.1094	46.85	60.64	58.67	48.59	
$\text{Cs}_2\text{O} \cdot 2\text{MoO}_3$	9	0.2277	0.1140	50.07	50.62	48.11	52.56	53.21
	10	0.2585	0.1330	51.45	50.62	48.15	53.86	

TABLE 2

Calcination of $\text{Me}_2\text{O} \cdot 2\text{MoO}_3$ Alloys at 1000° . Calcination time: 6 hours.

Composition of preparation	Test No.	Weight, grams	Loss of weight		Percentage of MoO_3		Loss of MoO_3	
			grams	Per cent	Before test	After test	Per cent of initial content	Mean value
$\text{Li}_2\text{O} \cdot 2\text{MoO}_3$	1	0.2081	0.0333	16.00	90.61	89.93	16.65	16.65
$\text{Na}_2\text{O} \cdot 2\text{MoO}_3$	2	0.2035	0.0081	3.98	82.28	82.09	4.18	4.14
	3	0.2129	0.0082	3.85	82.28	82.08	4.11	
$\text{K}_2\text{O} \cdot 2\text{MoO}_3$	4	0.2151	0.0152	7.07	75.35	75.04	7.46	7.47
	5	0.2230	0.0161	7.22	75.35	75.08	7.49	
$\text{Rb}_2\text{O} \cdot 2\text{MoO}_3$	6	0.2089	0.0169	8.09	60.64	60.11	8.92	9.15
	7	0.2091	0.0178	8.51	60.64	60.07	9.38	
$\text{Cs}_2\text{O} \cdot 2\text{MoO}_3$	8	0.2075	0.0204	9.83	50.62	49.87	11.14	11.30
	9	0.2038	0.0215	10.32	50.62	49.94	11.47	

In view of the fact that the loss of weight was much higher than in the alloys with a composition of $\text{Me}_2\text{O} \cdot 2\text{MoO}_3$ we ran the tests for 4 hours. Again, the maximum loss of molybdic anhydride occurred in the lithium preparation (65.76%) dropping to 30.69% for the sodium compound and reaching a minimum for the alloy $\text{K}_2\text{O} \cdot 3\text{MoO}_3$ (16.78%). The alloys of rubidium and cesium molybdates, with a composition of $\text{Me}_2\text{O} \cdot 3\text{MoO}_3$, again exhibit an increased loss of MoO_3 (21.46 and 23.11%, respectively).

We had to limit the calcination of alloys with the composition of $\text{Me}_2\text{O} \cdot 4\text{MoO}_3$ to 2 hours, as they suffered an even greater loss of MoO_3 than the preceding alloys.

The loss of molybdic anhydride was least for the cesium preparation (10.3%), rising progressively as we passed to the molybdates of rubidium, potassium, sodium, and lithium. The latter displayed a maximum loss of weight and MoO_3 loss (Table 4).

TABLE 3

Calcination of $\text{Me}_2\text{O} \cdot 3\text{MoO}_3$ Alloys at 1000° . Calcination Time: 4 hours.

Composition of preparation	Test No.	Weight, grams	Loss of weight		Percentage of MoO_3		Loss of MoO_3	
			Grams	Per cent	Before test	After test	Per cent of initial content	Mean value
$\text{Li}_2\text{O} \cdot 3\text{MoO}_3$	1	0.2101	0.1334	63.49	93.50	88.14	65.48	65.76
	2	0.2003	0.1282	64.00	93.50	88.23	66.04	
$\text{Na}_2\text{O} \cdot 3\text{MoO}_3$	3	0.2008	0.0558	27.79	87.41	84.62	30.79	30.69
	4	0.2006	0.0555	27.67	87.41	84.73	30.59	
$\text{K}_2\text{O} \cdot 3\text{MoO}_3$	5	0.2086	0.0341	16.35	82.92	82.83	16.47	16.78
	6	0.1989	0.0338	17.02	82.92	82.87	17.10	
$\text{Rb}_2\text{O} \cdot 3\text{MoO}_3$	7	0.1935	0.0411	21.24	70.13	70.02	21.37	21.46
	8	0.1912	0.0409	21.39	70.13	70.13	21.55	
$\text{Cs}_2\text{O} \cdot 3\text{MoO}_3$	9	0.1741	0.0394	22.63	60.51	60.27	22.88	23.11
	10	0.1671	0.0384	22.61	60.51	60.19	23.34	

TABLE 4

Calcination of $\text{Me}_2\text{O} \cdot 4\text{MoO}_3$ Alloys at 1000° . Calcination Time: 2 hours.

Composition of preparation	Test No.	Weight, grams	Loss of weight		Percentage of MoO_3		Loss of MoO_3	
			Grams	Per cent	Before test	After test	Per cent of initial content	Mean value
$\text{Li}_2\text{O} \cdot 4\text{MoO}_3$	1	0.2168	0.1123	52.03	95.00	89.90	54.61	54.75
	2	0.2073	0.1085	52.34	95.00	89.93	54.90	
$\text{Na}_2\text{O} \cdot 4\text{MoO}_3$	3	0.2133	0.0654	30.68	90.27	86.21	33.77	33.78
	4	0.2203	0.0677	30.73	90.27	86.13	33.79	
$\text{K}_2\text{O} \cdot 4\text{MoO}_3$	5	0.2088	0.0440	21.07	85.89	82.40	24.26	24.16
	6	0.2201	0.0459	20.85	85.89	82.35	24.07	
$\text{Rb}_2\text{O} \cdot 4\text{MoO}_3$	7	0.2020	0.0218	10.79	75.48	72.70	14.10	13.96
	8	0.2031	0.0214	10.54	75.48	72.69	13.83	
$\text{Cs}_2\text{O} \cdot 4\text{MoO}_3$	9	0.2104	0.0143	7.13	66.33	63.95	10.46	10.31
	10	0.2000	0.0138	6.90	66.33	64.01	10.17	

Thus, when $\text{Me}_2\text{O} \cdot 2\text{MoO}_3$ alloys are calcined, it is the sodium preparation that loses the least molybdic anhydride. Of the $\text{Me}_2\text{O} \cdot 3\text{MoO}_3$ alloys, the most stable in this respect is the potassium salt. Lastly, in the $\text{Me}_2\text{O} \cdot 4\text{MoO}_3$ alloys, it is

the cesium compound that exhibits the smallest MoO_3 loss. The losses of molybdic anhydride in all the tested alloys are compared in Table 5, based on 2 hours of calcining.

TABLE 5

Loss of Molybdic Anhydride During Calcination of the Acid Molybdates of the Alkali Elements

Temperature: 1000°. Calcining Time: 2 Hours.

Sample Size: Approx. 0.2 g

Me ₂ O:MoO ₃ ratio in initial preparation	Molybdates ¹ percentage loss of MoO ₃ ¹				
	Li	Na	K	Rb	Cs
1:2	5.55	1.38	2.39	3.05	3.77
1:3	32.80	15.02	8.39	10.90	11.55
1:4	54.75	33.78	24.16	13.96	10.31

The experimental data listed in Tables 1-4 were recomputed so as to establish the composition of the volatilized portion of the preparations. The results of these computations are shown in Table 6.

The vaporization products of the $\text{Me}_2\text{O} \cdot 2\text{MoO}_3$ alloys have a higher percentage of molybdic anhydride than is required for the dimolybdates. Most of the tested alloys of this type lose their Me_2O and MoO_3 in ratios that range from 1: 2.4 to 1: 2.9 at 1000°.

TABLE 6

Ratio of Oxides in the Vaporization Products of Alloys of the Acid Molybdates of the Alkali Elements.

Sample Size: Approx. 0.2 g

Test temperature	Me ₂ O:MoO ₃ ratio in the original alloy	Oxide ratio in the vaporization products				
		Li ₂ O:MoO ₃	Na ₂ O:MoO ₃	K ₂ O:MoO ₃	Rb ₂ O:MoO ₃	Cs ₂ O:MoO ₃
1200°	1:2	1: 2.38	1: 2.24	1: 2.28	1: 2.21	1: 2.20
1000	1:2	1: 3.46	1: 2.87	1: 2.43	1: 2.58	1: 2.56
1000	1:3	1: 5.76	1: 7.74	1: 3.44	1: 3.12	1: 3.06
1000	1:4	1: 69.7	1: 65.6	1: 68.7	1: 77.0	1: 95.0

This ratio falls to 1:3.5 in the lithium preparation. If the alloys in question actually contain dimolybdates, their vaporization is paralleled by a breakdown of some of these compounds, resulting in an increase in the MoO_3 content of the vaporization products.

It is not impossible that the $\text{Me}_2\text{O} \cdot 2\text{MoO}_3$ alloys are complex mixtures containing, say, Me_2MoO_4 , $\text{Me}_2\text{Me}_2\text{O}_7$, and $\text{Me}_2\text{Mo}_3\text{O}_{10}$. The vaporization of the acid molybdates must then result in a relative decrease in the percentage of MoO_3 in the vaporization residue.

In the lithium and sodium preparations, the vaporization products of the $\text{Me}_2\text{O} \cdot 3\text{MoO}_3$ alloys are still more enriched with molybdic anhydride than is the case in the 1:2 alloys. Here the evaporated portion has the following content:

¹) The most stable alloys of the acid molybdates are framed.

$\text{Li}_2\text{O}:\text{MoO}_3 = 1:5.76$ and $\text{Na}_2\text{O}:\text{MoO}_3 = 1:7.74$. This phenomenon is evidently due to the instability of the lithium and sodium trimolybdates. The dimolybdates are apparently vaporized, though with an appreciable content of free molybdic anhydride.

The molybdates of potassium, rubidium, and cesium exhibit a different state of affairs, the composition of the vaporized portion being close to that of the original alloy and agreeing with the latter fairly precisely in the case of cesium molybdate. It must therefore be inferred that the trimolybdates of potassium, rubidium, and cesium possess the greatest stability at high temperatures, vaporizing at 1000° with practically no decomposition.

The behavior of $\text{Me}_2\text{O} \cdot 4\text{MoO}_3$ alloys is quite singular. When they are calcined, they give off nearly pure molybdic anhydride, the amount of alkali oxide passing off in the volatile compound being many times smaller than in the alloys with a composition of $\text{Me}_2\text{O} \cdot 3\text{MoO}_3$. As a result, the $\text{Me}_2\text{O}:\text{MoO}_3$ ratio in the vaporized products ranges from 1:65 to 1:95 in this instance.

If there are tetramolybdates present in the $\text{Me}_2\text{O} \cdot 4\text{MoO}_3$ alloys, they doubtless are not very stable thermally. It is likewise noteworthy that even the rubidium and cesium preparations do not vaporize their stable trimolybdates in this case. On the contrary, the loss of cesium oxide from the alloy in question is a minimum, compared with the preparations of the other alkali elements. We must therefore conclude that the vapors of molybdic anhydride interfere with the vaporization of even the stable trimolybdates during calcination.

We tested our conclusions regarding the behavior pattern prevailing in the changes of composition of the stable isopolymolybdates as follows. We prepared alloys of the acid molybdates with the mean composition of $\text{Me}_2\text{O} \cdot 5\text{MoO}_3$. Weighed samples of these preparations were then calcined to constant weight at 1000° .

The test was considered complete when the loss of weight during the last 2 hours was one-tenth of that during the first 2 hours of calcining. The tests lasted 10 to 12 hours in all. The analyses of the calcining residues are given in Table 7.

It may be regarded as certain that calcining yields a mixture of the dimolybdate and the normal molybdate as the most highly acid lithium molybdate alloys, with the dimolybdate in the case of sodium and the trimolybdates in potassium, rubidium, and cesium. It is apparent that the composition of these compounds reflects the relative stability of the isopolymolybdates of the alkali elements at high temperature. The most stable are the dimolybdates in the case of lithium and sodium, the thermal stability being higher for sodium compound. Potassium, rubidium, and cesium are characterized by the formation of stable trimolybdates, their thermal stability being least for potassium and highest for cesium.

These stability relationships are doubtless related to changes in the polarizing effect of the ions in the alkali element series. The lower the polarizing effect of the cation, the more complex the anion of the polymolybdate than can be stably associated with it, and the stabler the given compound type.

SUMMARY

1. A study has been made of the stability and volatility of the isopolymolybdates of the alkali elements.
2. It has been found that calcining alloys of the acid molybdates at 1000 and 1200° results in an appreciable loss of molybdic anhydride and in the

TABLE 7

Calcining $\text{Me}_2\text{O} \cdot 5\text{MoO}_3$ Alloys to Constant Weight

Temperature 1000°. Sample Size: 0.2 - 0.4 g

Preparation	Percentage of MoO_3 in the preparation		Appearance		Closest Composition of the residue
	Before the test	After the test	Original preparation	Calcining residue	
$\text{Li}_2\text{O} \cdot 5\text{MoO}_3 \dots$	95.95	87.92	Gray platelets	Hyaline amber-yellow mass	$\text{Li}_2\text{O} \cdot 1.5\text{MoO}_3$
$\text{Na}_2\text{O} \cdot 5\text{MoO}_3 \dots$	92.86	82.47	ditto	Yellow acicular crystals	$\text{Na}_2\text{Mo}_2\text{O}_7$
$\text{K}_2\text{O} \cdot 5\text{MoO}_3 \dots$	88.41	83.94	Light-gray prisms	Minute pale-yellow crystals	$\text{K}_2\text{Mo}_3\text{O}_{10}$
$\text{Rb}_2\text{O} \cdot 5\text{MoO}_3 \dots$	79.38	71.54	ditto	ditto	$\text{Rb}_2\text{Mo}_3\text{O}_{10}$
$\text{Cs}_2\text{O} \cdot 5\text{MoO}_3 \dots$	71.86	59.97	ditto	ditto	$\text{Cs}_2\text{Mo}_3\text{O}_{10}$

evaporation of certain molybdates.*

3. The minimum overall loss of molybdenum from the $\text{Me}_2\text{O} \cdot 2\text{MoO}_3$ alloys occurs in the sodium compounds, from the $\text{Me}_2\text{O} \cdot 3\text{MoO}_3$ alloys in the potassium compounds, and from the $\text{Me}_2\text{O} \cdot 4\text{MoO}_3$ alloys in the cesium compounds.

4. The $\text{Me}_2\text{O}:\text{MoO}_3$ ratio ranges from 1:2.2 to 1:2.9 in the vaporization products of $\text{Me}_2\text{O} \cdot 2\text{MoO}_3$ alloys of the acid molybdates. Only in the lithium preparation does this reach drop to 1:3.46 at 1000°.

5. The $\text{Me}_2\text{O} \cdot 3\text{MoO}_3$ alloys contain extremely unstable compounds of lithium and sodium. The composition of the vaporizing portion is governed by the following ratios at 1000°: $\text{Li}_2\text{O}:\text{MoO}_3 = 1:5.8$; $\text{Na}_2\text{O}:\text{MoO}_3 = 1:7.7$.

6. The trimolybdates of potassium, rubidium, and cesium are vaporized with practically no decomposition.

7. Practically nothing but molybdic anhydride vaporizes from $\text{Me}_2\text{O} \cdot 4\text{MoO}_3$ alloys.

8. When $\text{Me}_2\text{O} \cdot 5\text{MoO}_3$ alloys are calcined to practically constant weight at 1000°, they yield the following residues: $\text{Li}_2\text{O} \cdot 1.5\text{MoO}_3$, $\text{Na}_2\text{Mo}_2\text{O}_7$, $\text{K}_2\text{Mo}_3\text{O}_{10}$, $\text{Rb}_2\text{Mo}_3\text{O}_{10}$ and $\text{Cs}_2\text{Mo}_3\text{O}_{10}$.

9. The dimolybdates of lithium and sodium, and the trimolybdates of potassium, rubidium, and cesium are most stable at 1000-1200°. The stability of the compounds rises in each isopolymolybdate series with an increase in the ionic radius of the alkali element.

LITERATURE CITED

- [1] Vikt. I. Spitsyn and I. M. Kuleshov, JGC 21, 408 (1951).¹ [2] Vikt. I. Spitsyn and I. M. Kuleshov, JGC 21, 1549 (1951).² [3] Vikt. I. Spitsyn and I. M. Kuleshov, JGC 21, 401 (1951).³

Received October 11, 1949.

Laboratory of Inorganic Chemistry,

¹) See C.B. English translation, p.445. The M. V. Lomonosov State University of Moscow.
²) As above, p. 453. ³) As above, p. 1701.

THE ADIAGONAL RECIPROCAL SYSTEM CONSISTING OF CALCIUM AND BARIUM FLUORIDES AND CHLORIDES

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If a compound is formed along one of the binary sides bounding the composition square of a reciprocal system, a reaction involving the formation of a compound will occur in the reciprocal system alongside the exchange reaction [1].

When the thermochemical effects of the exchange reaction are large, the reaction involved in the formation of a compound along one of the sides of the diagram may not affect the course of the exchange reaction perceptibly [2]. We then get the usual type of diagonal reciprocal systems (Figure 1,a), in which the initial triangulation of the reciprocal system's square is followed by a secondary adiaagonal triangulation, originating at the point in the diagram corresponding to the composition of the compound (Figure 1,b)[4,7]. This yields a diagonal system with a subordinate adiaagonal section.

When the reaction involved in the formation of a compound predominates, however, the triangulation of the composition square begins at the compound vertex, running to the vertex of one of the opposite constituents (adiaagonal secant (Figure 2,a) [1,4,6,7]). The secondary triangulation of the tetragon cut out by the adiaagonal secant may then take place along one of the diagonals of this tetragon [6]. When the reaction involving the formation of a compound predominates markedly, the secondary triangulation will again start at the compound vertex (second adiaagonal secant (Figure 2,b)). When the exchange reaction predominates within the tetragon, the secondary triangulation will occur along a diagonal (Figure 2,c). In the first case we have a completely adiaagonal triangulation of the square representing the reciprocal system by two adiaagonal triangulating secants (Figure 2,b). In the second case we get an adiaagonal system with a subordinated diagonal section (Figure 2,c).

In the three-dimensional diagram of the reciprocal system the energy predominance of one section or the other is manifested in the predominance of three-dimensional ridges. We may therefore speak of the pre-eminent position of one section, represented by a high ridge, as compared to that of another section, which may be represented by a slight ridge or even not represented at all by independent geometrical elements in the three-dimensional diagram.

In the kinds of systems we have considered (Figures 1 and 2) the triangulating sections may have the shape of binary systems or not. If the triangulating secant intersects at some point the field of the exchange reaction product that is first to separate from the melt but then vanishes again during cooling, owing to further interaction with the remaining molten mass, the solidified alloy will end up with only those two solid phases that are represented by the vertices of the triangulating secant.

The foregoing statements are illustrated in fluoride-chloride reciprocal systems.

The fluorides and chlorides of the alkali-earth elements combine to form sharply marked coordination compounds of the double-salt type, such as :

$\text{CaF}_2 \cdot \text{CaCl}_2$ (Figure 4); $\text{SrF}_2 \cdot \text{SrCl}_2$; and $\text{BaF}_2 \cdot \text{BaCl}_2$ (Figure 4). A number of reciprocal systems have been investigated for each of these compounds. Inasmuch as the thermal effects of the exchange reaction vary over a wide range in fluoride-chloride systems, this series of systems comprises all system types, ranging from the singular type to the purely adiaagonal.

When the exchange reaction involves very large amounts of heat, for instance, we get singular irreversible reciprocal systems:

Na, Ca || F, Cl — 24.36 Cal (Bergman, Banashek, and Bukhalova [3]),

K, Ca || F, Cl — 39.30 Cal (Bergman, Krauze [9]),

whereas when the exchange reaction heat is somewhat smaller, we get systems of the diagonal type, in which the ridge of the diagonal section is higher in the three-dimensional diagram than the ridge starting at the vertex of the coordination compound:

Na, Sr || F, Cl — 15.89 Cal (Bukhalova, Bergman [8]),

K, Ba || F, Cl — 22.32 Cal (Banashek, Bergman [10]),

Rb, Ba || F, Cl — 26.30 Cal (Banashek [11]).

When the heat evolved is of ordinary magnitude, we get adiaagonal systems with a subordinated triangulating diagonal:

Ca, Ba || F, Cl — 16.89 Cal (Bukhalova, Bergman¹),

Li, Ba || F, Cl — 13.22 Cal (Banashek, Bergman [14]).

When little heat is evolved in the exchange reactions, we get adiaagonal systems with two adiaagonal secants:

Li, Sr || F, Cl — 4.71 Cal (Banashek, Bergman),

Na, Ba || F, Cl — 7.38 Cal (Banashek, Bergman [14]).

This brief survey of several fluoride-chloride systems is a vivid illustration of the relationships between the magnitude of the heat evolved in the exchange reaction and in the reaction involving the formation of a compound and the geometrical configuration of the structural diagram.

The structural diagrams of a transitional nature, such as the Ca, Ba || F, Cl reciprocal system discussed in the present paper (Figure 3) — an adiaagonal system with a subordinate binary diagonal, are of especial interest.

EXPERIMENTAL

Procedure. The research was conducted by the visual polythermal method in a platinum crucible fitted with a platinum stirrer. The interior of the electric furnace was illuminated by a bright light source to obliterate the light radiated by the molten salts. We utilized a Pt/PtRh thermocouple with a highly sensitive Siemens-Halske galvanometer. The original CaCl_2 and BaCl_2 chlorides ("chemically pure" brands) were recrystallized twice; the fluorides were prepared from double-distilled hydrofluoric acid and carbonates prepared from the recrystallized chlorides. The melting points were taken as follows:

CaCl_2 : 773°; BaCl_2 : 962° (measured); CaF_2 : 1411°; BaF_2 : 1280° (not determined).

The experiments were run at 1100°.

¹) Data set forth in the present paper.

Binary systems (Figure 4, Table 1).

1. $\text{CaCl}_2 - \text{CaF}_2$ has been investigated by Nacken [15] and Plato [16], who found that a 1:1 incongruent compound was formed. We repeated this system. The eutectic point is located at 650° and 29.5% CaF_2 , the transition point lying at 735° and 42.5% CaF_2 .

2. $\text{BaCl}_2 - \text{BaF}_2$ has been investigated by Plato [16] and Winter. The system contains the congruent compound $\text{BaF}_2 \cdot \text{BaCl}_2$, which fuses at 1008° , and two eutectic points: 854° and 19% BaF_2 , and 936° and 74% BaF_2 .

Our data [4,5,21] differ only in exhibiting a homeomorphic transition point at 940° and 29% BaF_2 on the line for the compound $\text{BaF}_2 \cdot \text{BaCl}_2$. Bergman's and Banashek's thermodifferential analysis, in contrast to Plato's data, give no indication of the existence of solid solutions in the system.

3. $\text{CaCl}_2 - \text{BaCl}_2$ has been investigated by various authors: Sandonnini [17] and Ruff and Plato [18] indicate a simple eutectic system, while Schaefer [19] states that an incongruent compound is present.

TABLE 1

$\text{CaCl}_2 - \text{CaF}_2$		$\text{BaCl}_2 - \text{BaF}_2$		$\text{CaCl}_2 - \text{BaCl}_2$		$\text{CaF}_2 - \text{BaF}_2$	
Mol. % CaF_2	t°	Mol. % BaF_2	t°	Mol. % BaCl_2	t°	Mol. % CaF_2	t°
0	773	0	958	0	773	0	1280
4	742	10	900	10	730	35	1100
8	720	20	877	20	686	40	1060
12	696	24	913	25	663	45	1032
16	670	28	936	28	645	50	1022
20	658	32	960	31	626	55	1030
24	687	40	995	34	614	60	1056
28	700	50	1008	37	597	65	1083
32	713	60	997	40	607	100	1411
36	725	70	955	43	616	Minimum at 1022° , 50% CaF_2	
40	730	74	936	49	626		
44	788	80	1017	52	626		
48	833	100	1280	55	683	Points of inter- section: 954° , 36% BaCl_2 , 624° , 53.5% BaCl_2	
Points of inter- section: 650° , 19.5% CaF_2 ; 735° , 42.5% CaF_2		Points of inter- section: 845° , 18.5% BaF_2 ; 936° , 74% BaF_2		58	729		
				61	751		
				67.5	800		
				85	888		
				100	962		

Our figures differ fundamentally from those of the authors cited. We have found a congruent compound $\text{CaCl}_2 \cdot \text{BaCl}_2$, with a melting point of 629° . The eutectics are located at 594° and 36.5% BaCl_2 , and 624° and 54% BaCl_2 .

4. $\text{CaF}_2 - \text{BaF}_2$. According to Japanese authors [20] this system forms continuous solid solutions with a minimum on the fusibility curve at 50% BaF_2 and 1277° . According to our data, this fusibility minimum is located at 50% BaF_2 and 1022° .

Crystallization Surface in the Ternary Reciprocal System Ca, Ba || F, Cl

We made a study of 13 internal sections (Figure 5), represented in Tables 2, 3, 4, and 5 and in Figures 7, 8, and 9, as well as of the diagonal sections

$\text{CaF}_2 - \text{BaCl}_2$ and $\text{BaF}_2 - \text{CaCl}_2$ (Figure 6 and Table 2) and the section $\text{CaF}_2 - \text{BaF}_2 \cdot \text{BaCl}_2$ (Figure 5 and Table 2) in our investigation of the crystallization surface of this system. The basic data on the points of intersection of the curves are listed in each table.

The data for the lateral binary systems, the internal sections, and the projection on the $\text{CaCl}_2 - \text{BaCl}_2$ side (Figure 10) enable us to determine the configuration of the crystallization surface in this reciprocal system with satisfactory accuracy. The surface of crystallization consists of seven areas; in the BaCl_2 area we have the field subdivided into α - and β -heteromorphic varieties, while in the $\text{BaF}_2 \cdot \text{BaCl}_2$ area the homeomorphic transformation manifested at 940° at the $\text{BaF}_2 - \text{BaCl}_2$ binary sides was not exhibited very clearly owing to the steep slope of this area in the system.

TABLE 2

Diagonal		Diagonal		Adiagonal section		Section I	
$\text{BaCl}_2 - \text{CaF}_2$		$\text{CaCl}_2 - \text{BaF}_2$		$\text{BaF}_2 \cdot \text{BaCl}_2 - \text{CaF}_2$		$\left. \begin{matrix} 25\% \text{ CaF}_2 \\ 75\% \text{ BaCl}_2 \end{matrix} \right\} \rightarrow \text{BaCl}_2$	
Mol. % CaF_2	t°	Mol. % BaF_2	t°	Mol. % CaF_2	t°	Mol. % BaCl_2	t°
0	958	0	773	0	1008	0	690
5	902	5	693	7	996	10	676
10	875	10	629	11	985	20	667
15	840	14	636	20	960	30	657
20	811	18	663	28	935	35	651
25	817	22	683	34	959	40	645
30	857	26	709	Intersection point: $935^\circ, 28\% \text{ CaF}_2$			
35	891	30	760				
40	916	34	823				
45	948	38	873				
50	970	42	910				
Intersection point: $791^\circ, 22.5\% \text{ CaF}_2$		46	938	Intersection point: $644^\circ, 40.5\% \text{ BaCl}_2$			
		50	959				
		54	979				
		66	858				
		73	910				
		82	888				
		Intersection point: $611^\circ, 10\% \text{ BaF}_2$ $696^\circ, 25.5\% \text{ BaF}_2$ $910^\circ, 73\% \text{ BaF}_2$ $888^\circ, 82\% \text{ BaF}_2$					

Composition and Temperature of the System's Covariant Points:

	T°	Composition, mol. %	Phases in equilibrium
E I	880	$21\text{CaF}_2 + 17\text{BaCl}_2 + 62\text{BaF}_2$	$\text{CaF}_2 + \text{BaF}_2 + \text{BaF}_2 \cdot \text{BaCl}_2$
E II	776	$17.5\text{CaF}_2 + 76\text{BaCl}_2 + 6.5\text{BaF}_2$	$\text{CaF}_2 + \text{BaCl}_2 + \text{BaF}_2 \cdot \text{BaCl}_2$
E III	542	$3.5\text{CaF}_2 + 34\text{BaCl}_2 + 62.5\text{CaCl}_2$	$\text{CaCl}_2 + \text{CaF}_2 \cdot \text{CaCl}_2 + \text{CaCl}_2 \cdot \text{BaCl}_2$
P I	662	$17\text{CaF}_2 + 40.5\text{BaCl}_2 + 42.5\text{CaCl}_2$	$\text{CaF}_2 + \text{BaCl}_2 + \text{CaF}_2 \cdot \text{CaCl}_2$
P II	592	$8\text{CaF}_2 + 38\text{BaCl}_2 + 54\text{CaCl}_2$	$\text{BaF}_2 \cdot \text{BaCl}_2 + \text{BaCl}_2 + \text{CaCl}_2 \cdot \text{BaCl}_2$
e ₁	936	$28.5\text{CaF}_2 + 36\text{BaCl}_2 + 35.5\text{BaF}_2$	$\text{CaF}_2 + \text{BaF}_2 \cdot \text{BaCl}_2$
e ₂	791	$22\text{CaF}_2 + 78\text{BaCl}_2$	$\text{CaF}_2 + \text{BaCl}_2$

TABLE 3

Section II		Section III		Section IV		Section V	
30% BaCl ₂ → BaF ₂		40% BaCl ₂ → CaF ₂		40% BaCl ₂ → BaF ₂		50% CaCl ₂ → BaF ₂	
70% CaCl ₂		60% CaCl ₂		60% CaCl ₂		50% BaCl ₂	
Mol. %	t°	Mol. %	t°	Mol. %	t°	Mol. %	t°
BaF ₂		CaF ₂		BaF ₂		BaF ₂	
0	621	0	608	0	608	0	611
2	580	3	599	1	605	5	709
6	575	6	581	2	605	10	730
10	634	10	599	3	605	15	746
14	671	14	620	4	605	20	768
18	726	18	647	5	605	25	817
22	729	22	660	7.5	650	30	860
Point of inter- section: 544°, 4% BaF ₂ 650°, 13% BaF ₂ 684°, 17% BaF ₂		26	690	10	674	35	887
		30	739	15	702	40	903
		35	781	20	740	45	906
		Point of inter- section: 573°, 8% CaF ₂ 676°, 25% CaF ₂		25	814	50	923
30	860			55	944		
35	908			Point of inter- section: 755°, 19% BaF ₂ 906°, 47% BaF ₂			
Point of intersection: 605°, 5.5% BaF ₂ 720°, 19% BaF ₂							

TABLE 4

Section VI		Section VII		Section VIII		Section IX	
15% $\text{CaCl}_2 \rightarrow \text{BaF}_2$		5% $\text{BaF}_2 \rightarrow \text{CaF}_2$		75% $\text{BaCl}_2 \rightarrow \text{CaF}_2 \cdot \text{CaCl}_2$		25% $\text{BaF}_2 \rightarrow \text{CaF}_2$	
85% BaCl_2		75% BaCl_2		25% BaF_2		75% BaCl_2	
Mol. %	t°	Mol. %	t°	Mol. %	t°	Mol. %	t°
BaF_2		CaF_2		$\text{CaF}_2 \cdot \text{CaCl}_2$		CaF_2	
0	888	0	920	0	920	0	920
10	861	5	895	10	896	10	918
15	853	10	847	15	878	15	914
20	813	15	807	20	851	20	905
25	853	19	787	25	861	25	900
30	896	23	821	30	880	30	925
35	928	27	850	Point of inter- section: 842°, 21% $\text{CaF}_2 \cdot \text{CaCl}_2$		35	961
40	961	31	889			Point of intersection: 896°, 27% CaF_2	
45	977	Point of inter- section: 783°, 18% CaF_2					
50	989						
55	997						
60	997						
65	978						
Point of inter- section: 809°, 21.5% BaF_2							

TABLE 5

Section X		Section XI		Section XII		Section XIII	
55% BaF ₂ } → CaF ₂		70% BaF ₂ } → CaF ₂		85% BaF ₂ } → CaF ₂		80% BaF ₂ } → BaCl ₂	
45% BaCl ₂		30% BaCl ₂		15% BaCl ₂		20% CaF ₂	
Mol.% CaF ₂	t°	Mol.% CaF ₂	t°	Mol.% CaF ₂	t°	Mol.% BaCl ₂	t°
0	1007	0	954	0	1167	10	942
5	994	10	932	15	1016	13	995
10	986	15	925	20	983	16	938
15	965	20	917	25	955	19	896
20	955	25	912	30	921	22	915
25	941	30	938	35	916	25	938
30	941	35	974	40	948	30	967
35	968	Point of intersection: 905°, 24.5% CaF ₂		45	980	35	980
40	999			50	1015	40	986
Point of inter- section: 931°, 38% CaF ₂				Point of intersection: 907°, 33.5% CaF ₂		45	986
						50	977
						Point of intersection: 888°, 18% BaCl ₂	



Fig. 1. Triangulation of ternary reciprocal systems.

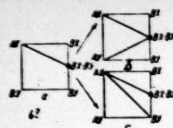


Fig. 2. Triangulation of reciprocal systems of the adagonal type.

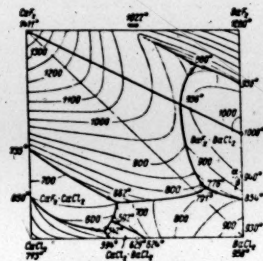


Fig. 3. Projection of the polytherms of a reciprocal system.

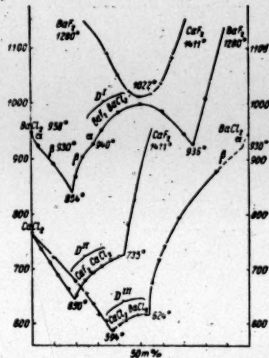


Fig. 4. Fusibility diagrams of binary systems.

Note: In Figures 3-10, the following symbols are used:
 $D^I = \text{BaF}_2 \cdot \text{BaCl}_2$; $D^{II} = \text{CaF}_2 \cdot \text{CaCl}_2$; $D^{III} = \text{CaCl}_2 \cdot \text{BaCl}_2$.

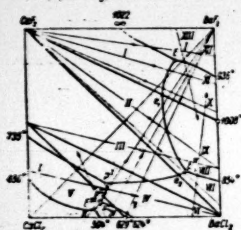


Fig. 5. Location of the internal sections through the system.

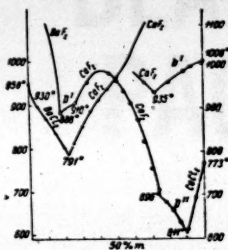


Fig. 6. Diagonal sections and the stable adagonal section $F \text{ BaF}_2 \cdot \text{BaCl}_2 - \text{CaF}_2$.

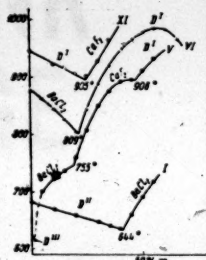


Fig. 7. Internal sections I, V, VI, and XI of the system.

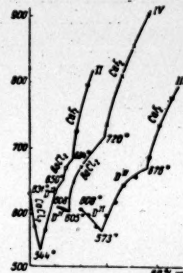


Fig. 8. Internal sections I, II, III, and IV of the system.

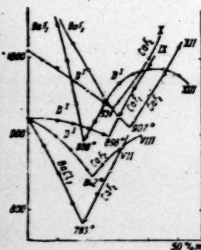


Fig. 9. Internal sections VII, VIII, IX, X, XIII and XIII of the system.

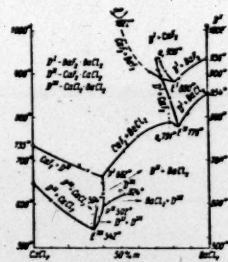


Fig. 10. Projection of the crystallization tree upon the $\text{CaCl}_2 - \text{BaCl}_2$ side.



Fig. 11. a - Photograph of a three-dimensional model of the Ca, Ba F, Cl system. b - Another view of the model.

The isotherms, plotted at 50° intervals, graphically indicate the relief of the areas, which is vividly shown in the photograph of the three-dimensional model (Figure 11, a, b).

The dimensions of the areas are given below, in per cent of the total area of the composition square:

CaF_2 — 55.1	$\text{BaF}_2 \cdot \text{BaCl}_2$ — 15.2
BaCl_2 — 11.3	$\text{CaCl}_2 \cdot \text{CaF}_2$ — 8.2
BaF_2 — 7.2	CaCl_2 — 2.7
	$\text{CaCl}_2 \cdot \text{BaCl}_2$ — 0.6

Interaction Between the System Components

There are compounds in three of the four binary systems that bound the composition square of the system Ca, Ba || F, Cl (Figure 3). Hence, the composition square of the reciprocal system will not be a simple quadrilateral, but a plane figure with seven vertices (the angle being 180° at the three derivative vertices for $\text{BaF}_2 \cdot \text{BaCl}_2$, $\text{CaF}_2 \cdot \text{CaCl}_2$, and $\text{CaCl}_2 \cdot \text{BaCl}_2$). It follows from the phase rule that for a chemical system (a system of the second class) consisting of seven constituents to remain a three-component system four chemical reactions must take place within it. And since the end result of each reaction in the reciprocal system is represented by a stable secant and corresponds to a triangulation, it follows that the given system may be subdivided into simplexes of four stable secants:

1) The $\text{BaF}_2 \cdot \text{BaCl}_2$ — CaF_2 section is the end result of the reaction:
 $2\text{BaF}_2 + \text{CaCl}_2 \rightarrow \text{BaF}_2 \cdot \text{BaCl}_2 + \text{CaF}_2$;

2) The BaCl_2 — CaF_2 section is the end result of the reaction:
 $\text{BaF}_2 + \text{CaCl}_2 \rightarrow \text{CaF}_2 + \text{BaCl}_2$;

3) The section $\text{CaF}_2 \cdot \text{CaCl}_2$ — BaCl_2 is formed as a result of the reaction: $\text{BaF}_2 + 2\text{CaCl}_2 \rightarrow \text{CaF}_2 \cdot \text{CaCl}_2 + \text{BaCl}_2$.

4) Lastly, the secant $\text{CaF}_2 \cdot \text{CaCl}_2$ — CaCl_2 corresponds to the reaction:
 $3\text{CaCl}_2 + \text{BaF}_2 \rightarrow \text{CaF}_2 \cdot \text{CaCl}_2 + \text{CaCl}_2 \cdot \text{BaCl}_2$

All the foregoing sections are shown in Figure 5. Two of these sections, $\text{BaF}_2 \cdot \text{BaCl}_2$ — CaF_2 and BaCl_2 — CaF_2 , are binary systems with valley eutectic points of 936 and 791°, respectively. The other two sections, $\text{CaF}_2 \cdot \text{CaCl}_2$ — BaCl_2 and $\text{CaF}_2 \cdot \text{CaCl}_2$ — $\text{CaCl}_2 \cdot \text{BaCl}_2$, are triangulating sections but are not binary systems. We may therefore regard this system, somewhat simplified, as an adiabagonal reciprocal system with a subordinated diagonal. The other two lateral compounds, $\text{CaF}_2 \cdot \text{CaCl}_2$ and $\text{CaCl}_2 \cdot \text{BaCl}_2$ have suppressed fields and actually affect the overall nature of the reciprocal system but little. The following interactions take place among the three compounds $\text{BaF}_2 \cdot \text{BaCl}_2$; $\text{CaF}_2 \cdot \text{CaCl}_2$, and $\text{CaCl}_2 \cdot \text{BaCl}_2$ within the reciprocal system:
 1) $\text{BaF}_2 \cdot \text{BaCl}_2 + \text{CaF}_2 \cdot \text{CaCl}_2 \rightarrow 2\text{BaCl}_2 + 2\text{CaF}_2$; 2) $\text{BaF}_2 \cdot \text{BaCl}_2 + \text{CaCl}_2 \cdot \text{BaCl}_2 \rightarrow 3\text{BaCl}_2 + \text{CaF}_2$; 3) $\text{CaF}_2 \cdot \text{CaCl}_2 + \text{CaCl}_2 \cdot \text{BaCl}_2$ — no reaction takes place.

In the first two reactions the compounds interact to form components of a stable diagonal section.

SUMMARY

1. The visual polythermal method has been employed in an investigation of the reciprocal system Ca, Ba || F, Cl, which has a single compound on each of three sides.

2. Owing to the prominent high-melting compound $\text{BaF}_2 \cdot \text{BaCl}_2$ (1008°) and the moderate heat of reaction in the exchange reaction (16.89 Cal), the reaction involving the formation of the compound $\text{BaF}_2 \cdot \text{BaCl}_2$ predominates over the exchange reaction in this reciprocal system. The reciprocal system is therefore an adiaxonal one, with a subordinated binary diagonal section.

3. The valley eutectic point of the adiaxonal stable section $\text{BaF}_2 \cdot \text{BaCl}_2$ — CaF_2 at 936° is higher than the valley eutectic point for the diagonal section CaF_2 — BaCl_2 at 791° .

4. The chemical interactions between the compounds formed on the sides of the reciprocal system have been considered.

LITERATURE CITED

- [1] A. G. Bergman, Coll. Reports, Div. Chem. Sci., USSR Acad. Sci. (1945).
- [2] A. G. Bergman and N. S. Dombrovskaya, Jour. Russ. Chem. Soc. 61, 1451 (1929).
- [3] A. G. Bergman, E. I. Banashek, G. A. Bukhalova, and E. I. Speranskaya, Coll. Reports, Div. Chem. Sci., USSR Acad. Sci. (1944).
- [4] Ibid. loc. cit. (1945).
- [5] G. A. Bukhalova, loc. cit. (1945).
- [6] Ibid., loc. cit. (1947).
- [7] A. G. Bergman and G. A. Bukhalova, J. Gen. Chem. 20, 235 (1950).¹⁾
- [8] A. G. Bergman and G. A. Bukhalova, Coll. Reports, Div. Chem. Sci., USSR Acad. Sci. (1945).
- [9] I. E. Krauze and A. G. Bergman, Proc. USSR Acad. Sci. 30, 1, (1942).
- [10] E. I. Banashek and A. G. Bergman, Proc. USSR Acad. Sci. 57, 905 (1947).
- [11] E. I. Banashek, Bull. Phys. Chem. Anal. Sect, XVIII.
- [12] A. G. Bergman and E. I. Banashek, loc. cit., XIX.
- [13] This literature reference has been omitted in the original Russian. Pub.
- [14] E. I. Banashek and A. G. Bergman, Proc. USSR Acad. Sci. 56, 485 (1947).
- [15] Nacken, Miner. Geol., Pal., 545, (1912).
- [16] Plato, Z. phys. Ch., 58, 350 (1907).
- [17] Sandonnini, Gazz. ch. Ital., 44, I, 290 (1914).
- [18] Ruff, Plato, Ber., 36, 2357 (1903).
- [19] Schaefer, N. Jahrb. Miner. Geol., Pal., 1914, I, 15.
- [20] Tuseya, Mori, Imamura, J. Soc. Ch. Ind., Japan, 36, 175 (1933).
- [21] A. G. Bergman and assoc., Coll. Reports, Div. Chem. Sci., USSR Acad. Sci. (1947).

Received August 30, 1949.

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¹⁾ See Consultants Bureau
English translation, p. 245.

THE INTERACTION OF NITRATES AND NITRITES OF THE METALS OF THE FIRST AND SECOND GROUPS OF D. I. MENDELEEV'S PERIODIC SYSTEM IN THE MOLTEN STATE

III. RESEARCH ON THE TERNARY SYSTEM OF NITRATES OF BARIUM — POTASSIUM — SODIUM IN THE MOLTEN STATE

P. I. Protsenko and A. G. Bergman

In our preceding reports [1,2,3] we described ternary systems consisting of the nitrates of calcium — potassium — sodium and strontium — potassium — sodium. The present report sets forth the results of an experimental study of a ternary system of the nitrates of barium — potassium — sodium. The ternary system of the nitrates of barium — potassium — sodium and two of its three constituent binary systems, barium nitrate — potassium nitrate and barium nitrate — sodium nitrate had previously been investigated by Harkins and Clark [4]. A repetition of the investigation of the barium nitrate — potassium nitrate binary system undertaken by A. P. Rostkovsky [5] revealed considerable inaccuracy in the determinations of the melting points carried out by Harkins and Clark. According to Harkins and Clark, the eutectic of the foregoing system has a melting point of 311.9° , whereas A. P. Rostkovsky found the melting point of the eutectic to be 290° . According to Harkins and Clark the liquidus curve for barium nitrate rises steeply from the eutectic point, after which it changes direction sharply, rising slowly, almost horizontally, up to an ordinate corresponding to 70 equimolecular per cent of barium nitrate. According to A. P. Rostkovsky's researches, however, there is no point of inflection in the liquidus of barium nitrate, which rises extremely sharply from the eutectic point. The specified wide divergences between the results reported by Harkins and Clark and those reported by A. P. Rostkovsky posed for us the problem of making a careful study of the whole ternary system in connection with systematic research on salt equilibria in melts of nitrates of alkali and alkali-earth metals undertaken by one of the present authors.

Repeated measurements of the cited binary systems made by us indicated that the melts cannot be heated above $500-502^\circ$. At this temperature the molten nitrates begin to break down, evolving oxygen. In both fusion curves the liquidus curves are wholly smooth, without any points of inflection. Both of the binary systems constitute eutectics. In the barium nitrate — potassium nitrate system the eutectic point is located at 287° , 22.5 equimolecular per cent of barium nitrate, and 77.5 equimolecular per cent of potassium nitrate, which agrees rather closely with the figures given by A. P. Rostkovsky [5]¹. The eutectic is located at 294° and a composition of 12.5% of barium nitrate and 87.5% of sodium nitrate (Figure 1, Tables 1 and 2).

The third binary system of potassium nitrate — sodium nitrate has been investigated by many authors: Hissink [6], Briscoe and Madgin [7], Bergman and Vaksberg [8], and the present authors [1], so that there is no need to repeat its description here (Figure 1).

Ternary Sections

In accordance with the general principles underlying the thermal analysis

¹) Henceforth compositions will always be given in equimolecular per cent.

TABLE 2
(Eutectic Point: 294°)

Point No.	Equimolecular %		Temperature at which the initial crystals separate out	Point No.	Equimolecular %		Temperature at which the initial crystals separate out
	(NaNO ₃) ₂	Ba(NO ₃) ₂			(NaNO ₃) ₂	Ba(NO ₃) ₂	
1	100	0	308°	12	75	25	364°
2	97.5	2.5	305	13	72.5	27.5	384
3	95	5	302	14	70	30	392
4	92.5	7.5	300	15	65	35	406
5	90	10	297	16	60	40	421
6	87.5	12.5	294	17	55	45	440
7	86.5	13.5	297.5	18	50	50	456
8	85	15	312	19	45	55	474
9	82.5	17.5	330	20	40	60	486
10	80	20	345	21	35	65	502
11	77.5	22.5	353	22	30	70	517

Section IV 20% (KNO₃)₂ + 80% (NaNO₃)₂ → Ba(NO₃)₂ has two crystallization branches — a short branch for the isomorphous mixture of potassium and sodium nitrates, and a long, extremely steep branch for the crystallization of barium nitrate. The transition point is located at 264° and a composition of 7.5% Ba(NO₃)₂, 18.5% (KNO₃)₂, and 74% (NaNO₃)₂ (Figure 4 and Table 6).

Transferring the transition points to a concentration triangle and connecting them together yielded the line of joint crystallization of the three system components, which demarcates the crystallization area of barium nitrate from the area of solid solutions (Figure 2).

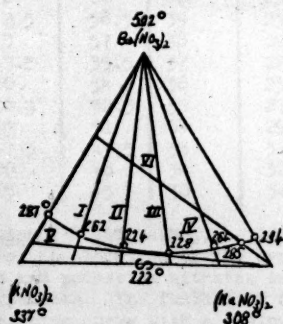


Fig. 2.

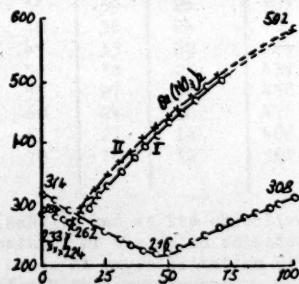


Fig. 3.

- I) 20% (NaNO₃)₂ → Ba(NO₃)₂;
80% (KNO₃)₂;
- II) 40% (NaNO₃)₂ → Ba(NO₃)₂;
60% (KNO₃)₂;
- V) 10% Ba(NO₃)₂ → (NaNO₃)₂.
90% (KNO₃)₂

TABLE 3

(Transition Point: 262°)

Point No.	Equimolecular %			Temp. at which the initial crystals separate out	Point No.	Equimolecular %			Temp. at which the initial crystals separate out
	Ba(NO ₃) ₂	KNO ₃	(NaNO ₃) ₂			Ba(NO ₃) ₂	KNO ₃	(NaNO ₃) ₂	
1	0	80	20	284°	11	30	56	14	347°
2	5	76	19	278	12	35	52	13	374
3	7.5	74	18.5	274	13	40	48	12	349
4	10	72	18	271	14	45	44	11	414
5	12.5	70	17.5	262	15	50	40	10	433
6	15	68	17	275	16	55	36	9	448
7	17.5	66	16.5	292	17	60	32	8	468
8	20	64	16	305	18	65	28	7	489
9	22.5	62	15.5	312	19	70	24	6	503
10	25	60	15	326					

TABLE 4

(Transition Point: 224°)

Point No.	Equimolecular %			Temp. at which the initial crystals separate out	Point No.	Equimolecular %			Temp. at which the initial crystals separate out
	Ba(NO ₃) ₂	KNO ₃	(NaNO ₃) ₂			Ba(NO ₃) ₂	KNO ₃	(NaNO ₃) ₂	
1	0	60	40	233°	11	30	42	28	364°
2	2.5	58.5	39	230	12	35	39	26	383
3	5	57	38	228	13	40	36	24	404
4	7.5	55.5	37	224	14	45	33	22	424
5	10	54	36	250	15	50	30	20	439
6	12.5	52.5	35	274	16	55	27	18	458
7	15	51	34	292	17	60	24	16	476
8	17.5	49.5	33	312	18	65	21	14	488
9	20	48	32	324	19	70	18	12	507
10	25	45	30	345					

Section V: 10% Ba(NO₃)₂ + 90% (KNO₃)₂ → (NaNO₃)₂ had as its objective determining the location of the eventual decomposition of the solid solutions of sodium and potassium nitrates in the various areas of crystallization of these components. The fusibility curve for Section V is a continuous crystallization curve with a minimum at 216° and a composition of 5.3% Ba(NO₃)₂, 49.7% (KNO₃)₂, and 45% (NaNO₃)₂. The Section V curve is typical of cases in which the components form an unbroken series of solid solutions. Section V exhibits no signs of any breakdown of the solid solutions (Figure 3 and Table 7).

Section VI 60% Ba(NO₃)₂ + 40% (KNO₃)₂ → (NaNO₃)₂ was investigated to corroborate the location of the line of joint crystallization plotted from the data for Sections I, II, III, and IV. This section has two crystallization branches — a long barium nitrate branch, which drops slowly at first and

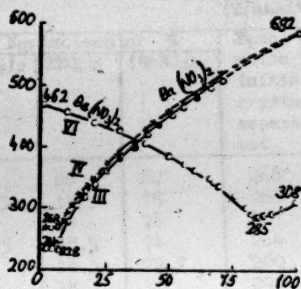


Fig. 4.

III) 60% $(\text{NaNO}_3)_2$ → $\text{Ba}(\text{NO}_3)_2$; IV) 80% $(\text{NaNO}_3)_2$ → $\text{Ba}(\text{NO}_3)_2$; 40% $(\text{KNO}_3)_2$ → 20% $(\text{KNO}_3)_2$
 → $\text{Ba}(\text{NO}_3)_2$; VI) 60% $\text{Ba}(\text{NO}_3)_2$ → $(\text{NaNO}_3)_2$ 40% $(\text{KNO}_3)_2$

then more rapidly to the transition point, and a short branch representing the crystallization of solid solutions of sodium and potassium nitrates.

The transition point of this section is located at 285° and a composition of 9.5% $\text{Na}(\text{NO}_3)_2$, 6.5% $(\text{KNO}_3)_2$, and 84% $(\text{NaNO}_3)_2$.

We were able to trace these sections up to 500-502°, with the sole exception of Section V. The molten salts began to break down violently above that temperature.

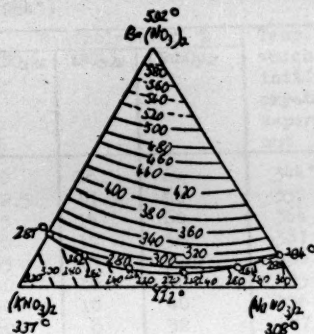


Fig. 5.

TABLE 5
(Transition Point: 228°)

Point No.	Equimolecular %			Temp. at which the initial crystals separate out	Point No.	Equimolecular %			Temp. at which the initial crystals separate out
	$\text{Ba}(\text{NO}_3)_2$	$(\text{KNO}_3)_2$	$(\text{NaNO}_3)_2$			$\text{Ba}(\text{NO}_3)_2$	$(\text{KNO}_3)_2$	$(\text{NaNO}_3)_2$	
1	0	40	60	234°	10	20	32	48	237°
2	2.5	38.5	59	232	11	25	30	45	360
3	5	37.8	57.2	229	12	30	28	42	380
4	6	37	57	228	13	35	26	39	400
5	7.5	36.5	56	244	14	40	24	36	418
6	10	35.8	54.2	276	15	45	22	33	436
7	12.5	34.5	53	298	16	50	20	30	448
8	15	33.8	51.2	313	17	60	16	24	480
9	17.5	32.5	50	321	18	70	12	18	510

The result of our experimental research on a ternary system consisting of the nitrates of barium — potassium — sodium have been summarized in the projection of the isotherm triangle of the three-dimensional structural diagram (Figure 5). The isotherms have been plotted at an interval of 20°. The ternary system of the nitrates of barium — potassium — sodium is

TABLE 6
(Transition Point: 264°)

Point No.	Equimolecular %			Temp. at which the initial crystals separate out	Point No.	Equimolecular %			Temp. at which the initial crystals separate out
	Ba(NO ₃) ₂	(KNO ₃) ₂	(NaNO ₃) ₂			Ba(NO ₃) ₂	(KNO ₃) ₂	(NaNO ₃) ₂	
1	0	20	80	268°	10	20	16	64	344°
2	2.5	19.5	78	266	11	22.5	15.5	62	355
3	5	19	76	265	12	25	15	60	364
4	7.5	18.5	74	264	13	30	14	56	387
5	9	18.3	72.7	280	14	35	13	52	406
6	10	18	72	290	15	40	12	48	425
7	12.5	17.5	70	306	16	50	10	40	456
8	15	17	68	320	17	60	8	32	487
9	17.5	16.5	66	332	18	70	6	24	517

interesting as a system that has only two crystallization areas and no ternary eutectic point. The largest crystallization area, the surface of which constitutes 82.05% of the entire area of the triangle, is that of barium nitrate. The other area with a crystallization surface of 17.95%, is the area for the isomorphous mixture of sodium and potassium nitrates.

The nature of the fusibility curves of the binary systems, viz: continuous solid solutions with a minimum in the potassium nitrate — sodium nitrate system, and eutectics without solid solutions in the two other binary systems, comprising the ternary system, served as a basis for the theoretical prediction of the crystallization area of barium nitrate, the crystallization area of potassium nitrate, the crystallization area of sodium nitrate, and the area of crystallization of the KNO₃ + NaNO₃ mix crystals adjoining the potassium nitrate — sodium nitrate side. Moreover, the curve of joint crystallization that separates the areas of the sodium and potassium nitrates should run from the ternary eutectic to the minimum, but gets lost somewhere in the crystallization area of the solid solutions, at the so-called critical blending point, without ever reaching the minimum. Adding the barium nitrate ought to cause the break-down of the solid solutions.

TABLE 7
(Transition Point: 216°)

Point No.	Equimolecular %			Temp. at which the initial crystals separate out	Point No.	Equimolecular %			Temp. at which the initial crystals separate out
	Ba(NO ₃) ₂	(KNO ₃) ₂	(NaNO ₃) ₂			Ba(NO ₃) ₂	(KNO ₃) ₂	(NaNO ₃) ₂	
1	10	90	0	314°	12	4.4	40.6	55	228°
2	9.2	85.8	5	302	13	4	36	60	237
3	8.8	81.2	10	290	14	3.5	31.5	65	248
4	8.2	76.8	15	278	15	3	27	70	257
5	7.7	72.3	20	266	16	2.5	22.5	75	206
6	7.3	67.7	25	253	17	2	18	80	216
7	7	63	30	240	18	1.5	13.5	85	284
8	6.3	58.7	35	230	19	1	9	90	274
9	6	54	40	223	20	0.5	4.5	95	300
10	5.3	49.7	45	216	21	0	0	100	308
11	5	45	50	218					

TABLE 8
(Transition Point: 285°)

Point No.	Equimolecular %			Temp. at which the initial crystals separate out	Point No.	Equimolecular %			Temp. at which the initial crystals separate out
	Ba(NO ₃) ₂	(KNO ₃) ₂	(NaNO ₃) ₂			Ba(NO ₃) ₂	(KNO ₃) ₂	(NaNO ₃) ₂	
1	60	40	0	462°	11	15	10	75	320°
2	54	36	10	450	12	12	8	80	300
3	48	32	20	335	13	10.5	7	82.5	290
4	42	28	30	420	14	9.5	6.5	84	285
5	36	24	40	402	15	9	6	85	287
6	30	20	50	382	16	7.5	5	87.5	291
7	27	18	55	370	17	6	4	90	294
8	24	16	60	360	18	3	2	95	300
9	21	14	65	345	19	0	0	100	308
10	18	12	70	335					

The decomposition of solid solutions by the addition of a third component has been confirmed in a number of systems previously investigated, as in Radishev's researches [5] on two ternary systems of the chlorides, bromides, and iodides of sodium and potassium, Brandt's researches [4] on systems of lead, potassium, and sodium chlorides, cadmium, potassium, and sodium bromides, etc.

The nature of the binary fusibility curves of this ternary system would lead us to expect the solid solution to decompose in our ternary system as well. A similar assumption apparently was held by Harkins and Clark, who classified this system as one of the ternary systems with a single invariant point, which they state is located at 214° and the following composition: 5% barium nitrate, 50% potassium nitrate, and 45% sodium nitrate. But, as we have said above, our careful experimental investigations yielded fusibility curves of another type - with two crystallization areas: a barium nitrate area and an area for the isomorphous mixture of potassium and sodium nitrates.

Palkin and Gromakov [5] made a similar observation in the sodium sulfate - sodium bromide - sodium chloride system, in which the solid solutions of sodium bromides and chlorides did not decompose.

Palkin and Gromakov [9] attribute the fact that a third component does not entail the decomposition of solid solutions, but rather is a stabilizing factor, to the melting point of the third component, which is higher than those of the two other components constituting the solid solutions. In the sodium sulfate - sodium bromide - sodium chloride system investigated by A. P. Palkin [9], for example, the melting points of the various components were as follows: Na₂SO₄ (Third component) 844°; NaBr 750°; and NaCl 800°.

In the system we investigated, Ba(NO₃)₂ melts with decomposition at 592°, KNO₃ at 337°, and NaNO₃ at 308°; that is, the melting point of the third component, Ba(NO₃)₂, is much higher than those of the components constituting the solid solutions, which agrees fully with the explanation suggested by A. P. Palkin.

Analyzing the above-mentioned papers by V. P. Radishev and Brandt, i.e.,

systems in which the third component causes the breakdown of the solid solutions, from this point of view. We find that the melting point of the third component is much below those of the other two in all such cases. In the ternary system of lead, sodium, and potassium chlorides, for example, the melting points of the several components are as follows: PbCl_2 (third component 495°), KCl 775° , and NaCl 798° . In this instance, lead chloride, with its lower melting point, manifests a sort of loosening action, resulting in the decomposition of the solid solutions. Figure 6 is an orthogonal projection of the crystallization paths upon the potassium nitrate - sodium nitrate side of the triangle.

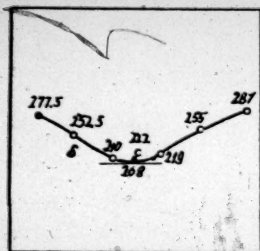


Fig. 6.

A characteristic feature of this ternary system is displayed in the crystallization tree. The curve of the joint crystallization of all three components is greatly bent, with a marked minimum, as is typical of solid solutions. It separates only two fields of crystallization - the area of pure barium nitrate and the area of the isomorphous mixture of potassium and sodium nitrates.

Comparison of the fusion curves of the binary systems studied by us (1,2,3) in the following series: $\text{Ca}(\text{NO}_3)_2 - (\text{NaNO}_3)_2$, $\text{Ca}(\text{NO}_3)_2 - (\text{KNO}_3)_2$, $\text{Sr}(\text{NO}_3)_2 - (\text{NaNO}_3)_2$, $\text{Sr}(\text{NO}_3)_2 - (\text{KNO}_3)_2$, $\text{Ba}(\text{NO}_3)_2 - (\text{NaNO}_3)_2$, $\text{Ba}(\text{NO}_3)_2 - (\text{KNO}_3)_2$, $\text{NaNO}_3 - \text{KNO}_3$ indicates that the ordinates of the eutectic's composition (and for the

last binary system, the minimum) are shifted toward the pure system component with a lower melting point, the greater the difference between the melting points, of the components constituting the eutectic or the minimum, the greater this displacement.

SUMMARY

1. A study has been made of the ternary system consisting of the nitrates of barium - potassium - sodium by the visual polythermal method.

2. The binary systems: 1) barium nitrate - sodium nitrate, and 2) barium nitrate - potassium nitrate have been defined more precisely; the former constitutes a eutectic at a temperature of 287° and a composition (in equimolecular %) of 22.5% barium nitrate and 77.5% sodium nitrate, the corresponding figures for the second system being 294° 12.5% barium nitrate, and 87.5% potassium nitrate.

3. It has been found, contrary to the assertions made by Harkins and Clark, that the ternary system of potassium, sodium, and barium nitrates does not have a ternary eutectic, but rather a minimum at a temperature of 216° , 5.4% barium nitrate, 46% sodium nitrate, and 48.6% potassium nitrate, being a system with two crystallization areas: with a crystallization area of 82.05% for barium nitrate and a crystallization area of 17.95% for an isomorphous mixture of potassium and sodium nitrates.

4. It has been shown that whenever two components form a eutectic or a minimum, the composition ordinates of the eutectic or of the minimum are shifted toward the ordinates of the pure component of the system with the lower melting point, the greater the difference between the melting points of the components constituting the given eutectic or minimum, the greater this shift.

LITERATURE CITED

- [1] P. I. Protzenko and A. G. Bergman, *J. Gen. Chem.* 20, 8, 1365 (1950)¹.
- [2] *Ibid.*, *J. Gen. Chem.* 21, 8 (1951).
- [3] P. I. Protzenko, *Report of the All-Union Chemical Soc.*, No. 2, p. 15 (1949).

¹) See Consultants Bureau English translation p. 1421.

²) See Consultants Bureau English translation p. 1509.

[4] Handbook of Physical, Chemical, and Engineering Constants, Vol. v, p. 143-201 Moscow (1930).

[5] Op. cit., Vol. VII, p. 190-192, Moscow (1931).

[6] Hissink, Z. phys. Chem., 32, 537 (1907).

[7] Brisco and Madgin, J. Chem. Soc., 123, 168 (1923).

[8] A. G. Bergman and N. M. Vaksberg, Bull. USSR Acad. Sci., Div. Chem. Sci. No. 1, 84 (1937).

[9] A. P. Palkin, S. D. Gromakov, and Assoc. Reactions with no solvent present, p. 7-14. Voronezh (1939).

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Received September 10, 1949.

THE TRANSFORMATIONS OF OLEFIN HYDROCARBONS IN THE PRESENCE OF METALIOSILICATE CATALYSTS

III. TRANSFORMATIONS OF SOME UNSATURATED HYDROCARBONS POSSESSING A QUATERNARY CARBON ATOM WITH AN ALUMINOSILICATE CATALYST¹⁾

R. D. Obolentsev and N. N. Gryazev

In a previous paper [1] dealing with the depolymerization of tri-isobutylene by aluminosilicates, one of the present authors noted that no explanation has yet been provided for the depolymerization of mono-olefin hydrocarbons. The results of the present research served as the basis for the supposition that tri-isobutylene can be depolymerized via the double-bond rule as well as via the stage in which a four-membered ring is formed. The latter procedure makes impossible the shift of the double bond from the middle of the carbon chain to either extremity.

Numerous references in the literature led Obryadchikov [2] to conclude that "olefins are isomerized by the displacement of the double bond within the molecule". In view of the reversibility of this shift of the double bond and of the difficulty of analyzing the liquid products of isomerization, we must regard the statement commonly found in the literature to the effect that catalysts including the aluminosilicates, can shift the double bond only within mono-olefin hydrocarbons as a misunderstanding. Actually, the depolymerization of 2,4,4-trimethylpentene-2 cannot be pictured as following the double-bond rule, so that the depolymerization reaction involving a four-membered ring is highly probable. When we remember the reversibility of the double-bond shift, the depolymerization of 2,4,4-trimethylpentene-1 by the double-bond rule leads to a decrease in its concentration, which ought to result in the isomerization of 2,4,4-trimethylpentene-2 into 2,4,4-trimethylpentene-1. Hence, the depolymerization of 2,4,4-trimethylpentene-2 does not yield an unequivocal answer in favor of one depolymerization reaction or the other. We cannot agree with Obryadchikov that ascertaining the behavior of 2,4,4-trimethylpentene-2 in depolymerization would solve the problem of the mechanism involved in the latter process. Nor can the extensive depolymerization of tri-isobutylene described in our paper mentioned above, which indirectly confirms the feasibility of depolymerization via a four-membered ring, provide a direct confirmation of the latter process.

S. V. Lebedev and I. A. Vinogradov-Volzhinsky [3] make the following statement in their proposal for a reaction involving the intermediate formation of a four-membered ring in the depolymerization of the dienes: "We do not claim that the proposed reaction pattern is absolutely certain, but we adopt it because it may be readily generalized and satisfactorily interprets our results both qualitatively and quantitatively." In a subsequent paper, S. V. Lebedev and N. A. Kudryavtsev [4] investigated the contact conversions of 3,3-dimethylbutene-1 and 4,4-dimethylpentene-2 with an aluminosilicate catalyst at 150-270°, apparently in order to confirm the pattern of decomposition via the intermediate formation of four-membered rings. S. V. Lebedev and N. A. Kudryavtsev were unable however, to demonstrate the intermediate formation of four-membered rings in these research subjects. This led S. N. Obryadchikov to conclude that S. V.

¹⁾ Cf. Sci. Papers, Saratov State Univ., 21, 142 (1949); J. Appl. Chem. 22, 157 (1949); 23, 1223 (1950). (For the latter reference, see C.B. English translation, p. 1299).

Lebedev and N. A. Kudryavtsev had not demonstrated this mechanism of the depolymerization of unsaturated hydrocarbons.

The objective of the present research has been to determine the reactions involved in the transformations of some unsaturated hydrocarbons with a quaternary carbon atom above an aluminosilicate catalyst. The substances used in this research were 3,3-dimethylbutene-1, 4,4-dimethylpentene-1, 2,3,3-trimethylbutene-1, and "di-isobutylene."

Various processes (cracking, isomerization, aromatization, etc.) take place during the catalytic transformations of unsaturated hydrocarbons with aluminosilicates, so that we were interested in determining their thermodynamic probability, even if only as a first approximation. We made thermodynamic calculations of various possible reactions in the catalytic conversions of the unsaturated hydrocarbons referred to above. In these calculations we were handicapped by the lack of various entropy values, specific heat capacities, heats of formation, and standard free energies of formation for some of the hydrocarbons under investigation and for the products of their transformation. Utilizing the relationships of changes between entropy, specific heat capacity, heat of formation, and standard free energy of formation to temperature and hydrocarbon structure [5, 6], we calculated the thermodynamic functions we required and computed the extent of equilibrium conversion for the decomposition and aromatization reactions (Fig. 1).

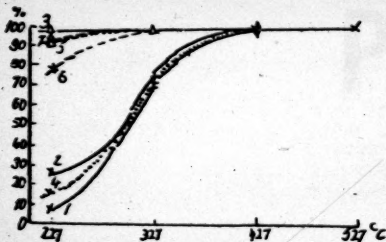


Fig. 1. % conversion as a function of temperature.

1 - 2,3,3-trimethylbutene-1 in ethylene and 2-methylbutene-2; 2 - 2,3,3-trimethylbutene-1 in isobutylene and propylene; 3 - 2,3,3-trimethylbutene-1 in toluene and hydrogen; 4 - 3,3-dimethylbutene-1 in isobutylene and ethylene; 5 - 3,3-dimethylbutene-1 in benzene and hydrogen; 6 - 4,4-dimethylpentene-1 in isobutylene and propylene; 7 - 4,4-dimethylpentene-1 in toluene and hydrogen.

Inspection of the curves shown in Fig. 1 leads us to conclude that the depolymerization of 3,3-dimethylbutene-1 with a percent conversion of practical interest may be effected only at a temperature in excess of 150°.

EXPERIMENTAL

Method of analysis. The gaseous products were subjected to low-temperature rectification in a "copper column". The individual gas fractions secured as the result of rectification were analyzed in an Orsat apparatus [7]. The liquid products - both the original ones and those secured as the result of catalytic cracking - were rectified in a column with a fractionating efficiency equivalent to 20 theoretical trays at complete reflux [8].

The bromine number of the liquid products was determined by the method described by G. D. Galpern and E. V. Vinogradova [9].

The percentage of aromatic hydrocarbons was determined by measuring the relative dispersion of light by the B. V. Ioffe method [10]. The percentage of unsaturated hydrocarbons with a tertiary carbon atom at the double bond was determined by the method described by B. L. Moldavsky and V. Zharkova [11]. We tested the method suggested by these authors with an artificial mixture

consisting of 90% "diisobutylene" by weight and 10% 4,4-dimethylpentene-1 by weight. We began by proving that the "diisobutylene" contained 95% of "tertiary" unsaturated hydrocarbons, while the 4,4-dimethylpentene-1 contained none of these "tertiary" unsaturated hydrocarbons. This mixture therefore should have contained 85.5% of "tertiary" unsaturated hydrocarbons. In one analysis we found 85.5%, and in a parallel run 84.5% of "tertiary" unsaturated hydrocarbons. The margin of error in this determination of these unsaturated hydrocarbons did not exceed 1% of absolute.

The structure of the liquid unsaturated hydrocarbons was determined by ozonidation and identifying the hydrolysis products of the ozonides. Ethyl chloride was used as the solvent for the substance to be ozonized, it being carried off in a stream of carbon dioxide at room temperature after ozonidation was complete. The ozonides were decomposed with ice, the structure of the hydrocarbons used for ozonidation being inferred from the analysis of the hydrolysis products of the ozonides.

Original products. 2,3,3-Trimethylbutene-1 was produced in several batches by dehydrating 2,3,3-trimethylbutanol-2 with 60% sulfuric acid, 70% sulfuric acid, and iodine. Best results were secured with 70% sulfuric acid (71% theoretical yield). 2,3,3-Trimethylbutanol-2 was prepared by the method described by V. M. Tolstopyatov [12]. The 2,3,3-trimethylbutene-1 secured by dehydrating the alcohol was fractionated into the column mentioned above, yielding 193.5 g of 2,3,3-trimethylbutene-1 with a b.p. of 77.5-78.5° (760 mm); d_4^{20} 0.7030; n_D^{20} 1.4016.

Mol. weight 97.7. Bromine number 162.7. 99.4% unsaturated hydrocarbons. 99.3% unsaturated hydrocarbons with a tertiary carbon atom attached to the double bond.

Data in the literature [13]: b.p. 78.0° d_4^{20} 0.7023; n_D^{20} 1.4020.

To prove the structure of the 2,3,3-trimethylbutene-1 2.4 g of the product was dissolved in 10 ml of ethyl chloride and ozonized. Ozonidation continued for 2.5 hours. Decomposition of the ozonide yielded an oily and an aqueous layer. The oxime of pinacolone was isolated from the former. The oxime had a m. p. of 74° after double recrystallization from methanol. A test sample mixed with the pure oxime of pinacolone had a m.p. of 74-74.5°. The semicarbazone of the pinacolone had the same temperature after several crystallizations from water (156.5°). A fusion mixture had a m.p. of 156.5-157°. Pinacolone was the only carbonyl compound found in the oily layer.

The aqueous layer exhibited a positive reaction for aldehydes with Schiff's solution. We secured formaldehydedimethone, which had a m.p. of 189.1° after triple recrystallization from alcohol. The melting point of a fusion mixture was 189.0°. The formaldehyde yield was 84.6% of the theoretical, based on 2,3,3-trimethylbutene-1. The yield of pinacolone was 89.8% of the theoretical. No other carbonyl compounds were found in the aqueous layer. This proved that we had secured an adequately pure 2,3,3-trimethylbutene-1.

3,3-Dimethylbutene-1 was prepared by the L. A. Chugayev [14] method: dehydrating pinacolyl alcohol via methyl xanthate. The slight departure from the procedure described in the literature [15] involved the preparation of the potassium alcoholate of pinacolyl alcohol by the direct reaction of metallic potassium with pinacolyl alcohol. In the foregoing procedure the potassium alcoholates of secondary alcohols are produced in an exchange reaction between the potassium alcoholate of tertiary amyl alcohol and the secondary alcohols. In our procedure we evidently were utilizing the forgotten demonstration by E. E. Vagner and V. O. Brikner [16] that metallic potassium does not isomerize secondary alcohols.

The 3,3-dimethylbutene-1 we prepared was purified by rectifying it with a

column. This yielded 22.1 g of 3,3-dimethylbutene-1, the yield being 58.0%, based on pinacolyl alcohol (Schurman and Boord [17] achieved a yield of 41.6%).

Characteristics of 3,3-dimethylbutene-1: b.p. 41-41.5° (760 mm); d_4^{20} 0.6522; n_D^{20} 1.3770

Mol. weight 84. Bromine number 189.0. 99.4% unsaturated hydrocarbons. 1.5% unsaturated hydrocarbons containing a tertiary carbon atom attached to the double bond.

Data in the literature [13]: b.p. 41.2° (760 mm); d_4^{20} 0.6519; n_D^{20} 1.3766.

4,4-Dimethylpentene-1 was synthesized by the method described by Whitmore and Homeyer [18]: from tert-butylmagnesium chloride and allyl bromide. We successfully used mercuric chloride as an activator in synthesizing tert-butylmagnesium chloride from tert-butyl chloride and metallic magnesium (fine shavings). The yield of 4,4-dimethylpentene-1 was 34.5% of the theoretical, based on allyl bromide. Rectification yielded 15.8 g of 4,4-dimethylpentene-1 with b.p. of 71.72° (760 mm); d_4^{20} 0.6821; n_D^{20} 1.3924.

Mol. weight 97.5. Bromine number 163. 99.3% unsaturated hydrocarbons. No "tertiary" unsaturated hydrocarbons were present. The analysis data indicate that we had secured satisfactorily pure 3,3-dimethylbutene-1 and 4,4-dimethylpentene-1.

Di-isobutylene. The raw material used was commercial di-isobutylene, which was subjected to cold sulfuric acid polymerization; double rectification yielded a fraction that boiled at 100-105°; d_4^{20} 0.7201; n_D^{20} 1.4131.

Mol. weight 113. Bromine number 140. 98.5% unsaturated hydrocarbons. 95.0% "tertiary" unsaturated hydrocarbons. The physical constants indicate that this is probably a 3:2 mixture of 2,4,4-trimethylpentene-1 and 2,4,4-tert-methylpentene-2.

Description of apparatus and experimental procedure. The tests were run in an apparatus of the flow type, differing from the equipment described previously [1] in that the liquid was fed from an automatic buret [19], with a low-temperature rectifying column [7] being added to the receiver to effect better separation of the liquids from the gaseous products.

The catalyst was activated and regenerated at 480-500° by passing air over it at the rate of 200-300 volumes per volume of catalyst per hour. After activation of the catalyst was complete, nitrogen was blown through the system. The runs lasted from 15 to 60 minutes. After the run was over, the liquefied gaseous products were subjected to low-temperature rectification, and the liquid products were weighed. We have called the weight of the liquid products plus the weight of the liquid residue of low-temperature rectification of the gas the "weight of catalyzate".

During regeneration the exhaust gas was analyzed for its carbon dioxide content every 3 minutes. Regeneration was stopped as soon as no more carbon dioxide was found in the exhaust gas. The percentage of carbon in the coke was determined from the amount of carbon dioxide evolved. Since the amount of hydrogen in the coke is low (no more than 8%), we took the % of carbon to be the amount of coke deposited on the catalyst. In all our runs the increase in weight of the reactor greatly exceeds the amount of coke found. This discrepancy is due to the fact that tarry products were deposited on the glass packing ahead of and behind the catalyst zone. We termed the difference between the added weight of the reactor during a run and the weight of the coke "reactor residue". Five runs were made with each sample of catalyst, after which it was replaced by a new one.

Catalytic cracking of di-isobutylene. The tests of the catalytic cracking of di-isobutylene were run in the 350-450° range at a rate of 0.75 volumes per volume of catalyst per hour. The stability of catalyst operation was checked by parallel runs. Some of our test results are listed in Table 1.

TABLE 1
Catalytic Cracking of Di-Isobutylene

(Volumetric rate = 0.75 vol. per catalyst vol. per hour;
Atmospheric pressure)

Test No.	14	12	9	10	15
Temperature °C	350	430	430	450	450
Length of run, minutes	40	30	30	40	30
Per cent by weight (of the initial product): Gas ...	31.7	41.0	40.5	48.2	46.0
Catalyzate	52.5	45.0	46.0	33.5	35.6
Coke	8.9	6.1	5.6	9.2	10.1
Reactor residue	3.3	5.5	4.9	4.6	5.5
Losses	3.6	2.4	3.0	4.5	2.8
Gas formation (mols per mol of charge)	0.555	-	0.972	-	1.192
Composition of gaseous products (per cent by volume):					
H ₂	1.6	-	1.1	-	0.1
CH ₄	5.7	-	10.5	-	10.7
C ₂ H ₄	1.9	-	1.1	-	1.3
C ₂ H ₆	0.3	-	0.2	-	1.9
C ₃ H ₈	8.4	-	18.6	-	29.2
C ₃ H ₆	2.7	-	3.4	-	4.7
iso-C ₄ H ₈	60.5	-	28.2	-	20.5
n-C ₄ H ₈	12.7	-	24.6	-	23.8
C ₄ H ₁₀	6.2	-	12.3	-	7.8
C _n H _{2n}	83.5	-	72.5	-	74.8
C _n H _{2n} + 2	14.9	-	26.4	-	25.1
Group chemical composition of the catalyzate (per cent by weight):					
Paraffin and naphthene hydrocarbons ¹	11.0	-	56.5	-	47.8
Aromatic hydrocarbons	None	-	None	-	1.7
Unsaturated hydrocarbons:					
Secondary	46.0	-	32.2	-	15.6
Tertiary	43.0	-	11.3	-	34.9

The figures in Table 1 indicate that raising the temperature results in the formation of more gas. The per cent of methane in the gas rises as the temperature is raised from 350 to 430°. A small quantity of hydrogen was found. The isobutylene formed by the decomposition of the di-isobutylene is probably isomerized to n-butylenes, an increase in temperature favoring this latter reaction. The presence of butanes in the gas may be attributed to the

¹ Here and in the succeeding tables the term paraffin and naphthene hydrocarbons covers the saturated residue, which most likely consisted of paraffin hydrocarbons.

fact that the isobutylene and *n*-butylenes are hydrogenated to isobutane and *n*-butane as the result of disproportionation of the hydrogen [23].

When the temperature is raised from 350° to 430°, the percentage of unsaturated hydrocarbons drops off, both in the gas and in the catalyzate. This is also related to the greater disproportionation of the hydrogen at 430°. Raising the temperature from 350° to 430° intensifies the isomerization processes. This is manifested by a decrease in the percentage of tertiary unsaturated hydrocarbons. A small amount of aromatic hydrocarbons was found in the catalyzate secured in the 450° run.

The resulting catalyzates were rectified in the same column utilized to isolate the initial products. Owing to the small amounts of catalyzate available, a mixture consisting of the catalyzates secured in parallel runs was fractionated. Table 2 indicates the yield and the group chemical composition of various fractions of the catalyzate.

The sharp drop in the percentage of tertiary unsaturated (which is the boiling point of the original di-isobutylene), hydrocarbons contained in the 100-105° fraction as compared with the original, is evidence of the vigorous isomerization of the original di-isobutylene. As the temperature is raised from 350° to 400°, the yield of the 100-105° fraction drops from 40 to 20%.

TABLE 2

Yield and Group Chemical Composition of the Various Catalyzate Fractions Secured in the Catalytic Cracking of Di-Isobutylene

(Volumetric rate: 0.75 vol. per vol. of catalyst per hour; Atmospheric pressure)

Test No.	14 and 21 (350°)			6 and 18 (400°)		
Fraction.	46-100°	100-105°	105°	50-100°	100-105°	105°
Yield (per cent of the catalyzate by weight)	25.2	40.0	34.8	31.2	20.0	48.8
Group chemical composition:						
Paraffin and Naphthene hydrocarbons ...	13.5	4.0	-	33.5	21.5	40.5
Aromatic hydrocarbons	None	None	-	None	None	None
Unsaturated hydrocarbons:						
Secondary	61.5	30.5	-	14.5	57.5	36.0
Tertiary	25.0	65.5	-	62.0	21.3	23.5

The data listed in Tables 1 and 2 were employed in calculating the per cent conversion of the di-isobutylene at various temperatures. Thus, in Tests 14 and 21, run at 350°, the per cent conversion was 85.5%, while it was 98.0% in Tests 6 and 18, run at 400°. We defined the per cent conversion as the difference between the amount of the original product and that of the unchanged product in the catalyzate (based on the initial raw material).

Catalytic cracking of 2, 3, 3-trimethylbutene-1. The 2, 3, 3-trimethylbutene-1 was passed over the aluminosilicate catalyst at 300, 350, 400 and 450° at a volumetric rate of 5 volume per volume of catalyst per hour. The test results are listed in Table 3.

TABLE 3

Catalytic Cracking of 3, 3-Dimethylbutene-1, 4, 4-Dimethylpentene-1,
and 2, 3, 3-Trimethylbutene-1(Volumetric rate: 0.5 vol. per catalyst volume per hour;
Atmospheric pressure)

Initial product	3,3-Di- methyl- butene-1	4,4-Di- methyl- pentene-1	2,3,3-Trimethylbutene-1					
Test No	33	32	27	31	25	26	23	24
Temperature °C....	400	400	300	350	400	400	450	450
Per cent by weight (of raw material):								
Gas	25.1	19.2	3.1	15.3	28.0	28.9	30.8	32.5
Catalyzate ..	62.0	59.6	86.9	78.0	65.7	64.0	58.6	57.0
Coke	3.9	13.2	1.7	1.9	1.9	1.5	3.5	3.0
Reactor residue	5.2	7.3	5.6	2.0	4.1	5.0	4.8	5.5
Losses	3.8	0.7	2.7	2.8	0.3	0.6	2.3	2.0
Gas formation (mols per mol of charge)	0.528	0.391	0.074	0.350	0.635	0.650	0.734	0.766
Composition of gaseous products (Per cent by vol- ume):								
H ₂	0.4	1.0	-	-	0.1	-	0.3	0.3
CH ₄	7.0	1.3	-	0.7	6.2	6.0	8.7	8.3
C ₂ H ₄	40.7	0.8	41.0	46.3	22.6	20.4	22.3	22.4
C ₂ H ₆	4.1	0.2	1.0	0.9	1.0	0.7	0.6	0.8
C ₃ H ₈	4.5	45.4	21.6	22.3	23.2	26.1	27.3	27.5
C ₃ H ₆	0.5	1.7	1.6	1.1	5.5	5.3	9.1	6.8
iso-C ₄ H ₈	25.3	33.8	19.6	12.5	12.4	12.7	12.1	13.3
n-C ₄ H ₈	10.6	12.0	12.4	15.5	17.3	15.8	13.4	15.1
C ₄ H ₁₀	6.9	3.8	2.8	0.7	11.7	13.0	6.2	5.5
C _n H _{2n}	81.1	92.0	94.6	96.6	75.5	75.0	75.1	78.3
C _n H _{2n} + 2 ...	18.5	7.0	5.4	3.4	25.4	25.0	24.6	21.4
Group chemical composition (per cent by weight):								
Paraffin and naphthene hydrocarbons	-	-	-	-	24.7	23.9	27.2	25.6
Aromatic hydrocarbons	-	-	-	-	None	None	1.6	2.0
Unsaturated hydrocarbons:								
Secondary	-	-	-	-	6.2	5.7	6.1	5.2
Tertiary	-	-	-	-	69.1	70.4	65.1	67.2
Per cent conver- sion	96.3	86.3	67.4	78.9	85.5		89.4	

We see from the figures in Table 3 that the catalyzate yield drops as the temperature is raised in the catalytic cracking of 2,3,3-trimethylbutene-1, while the yield of gas rises uninterruptedly. A large percentage of ethylene was found in the gaseous products (ranging from 46.3 to 20.4%). As in the cracking of

di-isobutylene, the *n*-butylenes produced in the decomposition of the 2,3,3-trimethylbutene-1 are apparently formed because of the isomerization of isobutylene. The increase in the percentage of the *n*-butylenes as the temperature is raised may be regarded as partial confirmation of this. The presence of butanes in the gaseous products and the data on the group chemical composition of the catalysis products are evidence of the disproportionation of hydrogen that occurs. The presence of a small amount of secondary unsaturated hydrocarbons in the catalyzate indicates that the 2,3,3-trimethylbutene-1 is only slightly isomerized.

Figure 2 shows the rectification curves of the catalytic products secured, while the group chemical composition of the resultant fractions is given in Table 4.

TABLE 4
Group Chemical Composition of the Various Fractions of the Catalysis Products Secured in the Catalytic Cracking of 2,3,3-Trimethylbutene-1

Test No. and temperature	Fraction No.	Fraction boiling point, °C	Per cent by weight			
			Paraffin and naphthene hydrocarbons	Aromatic hydrocarbons	Unsaturated hydrocarbons	
					Tertiary	Secondary
27 (300°)	1	55-75	34.2	None found	60.8	5.0
	2	75-80	35.5	ditto	63.1	1.4
	3	above 80	23.5	"	66.1	10.4
31 (350°)	1	38-40	3.5	None found	95.0	1.5
	3	56-57	5.8	ditto	90.2	4.0
	4	73-74	36.8	"	62.0	1.2
	5	77.5-79	34.1	"	60.0	5.9
	6	above 79	25.9	"	62.1	12.0
25 and 26 (400°)	1	38-40	6.8	None found	92.0	1.2
	3	55.5-56.5	8.7	ditto	85.4	5.9
	5	72-75	33.2	"	60.6	6.2
	7	77-81	34.7	"	64.8	0.5
	8	above 81	24.8	3.2	58.0	14.0
23 and 24 (450°)	1	37-42	8.3	None found	87.5	4.2
	3	56-56.5	7.8	ditto	82.3	9.9
	5	70-75	35.5	"	60.1	4.4
	7	77.5-80	38.2	"	60.4	1.4
	8	above 80	22.5	8.2	56.2	13.1

The figures in Table 4 show that the fractions whose boiling points are closest to that of the initial product are most effectively hydrogenated via disproportionation of hydrogen. Aromatic hydrocarbons were found in some fractions with higher boiling points than that of the initial product.

The data cited in Tables 3 and 4 and shown in Fig. 2 were utilized to calculate the per cent conversion of the 2,3,3-trimethylbutene-1 (Fig. 3).

The group chemical compositions of catalyzate fractions produced at different temperatures but with adjacent boiling points are very similar. This indicates that these fractions contain a large percentage of similar unsaturated hydrocarbons. Mixtures of these fractions were ozonidized in order to establish the structure of these unsaturated hydrocarbons,

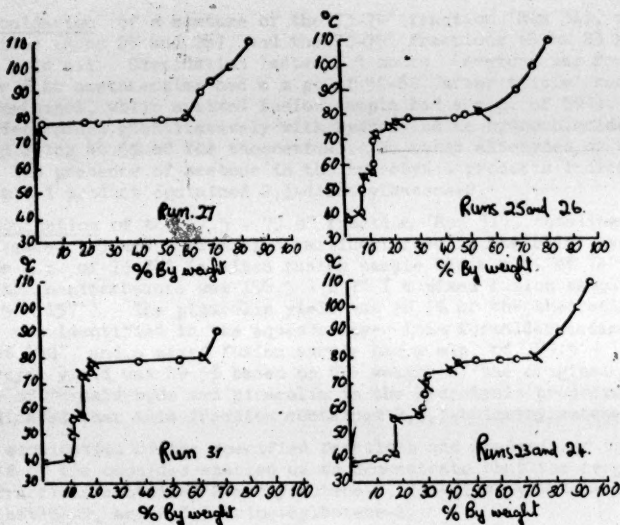


Fig. 2. Fractionation curves of the liquid products secured in the catalytic conversions of 2,3,3-trimethylbutene-1.

1. Ozonidation of a mixture of the 38-40° fractions (Runs 25, 26 and 31) and the 37-42° fractions (Runs 23 and 24). 2.1 g of the mixture employed. Ozonidation lasted only 15 minutes., after which the product was decomposed with ice. The resultant oily layer was not analyzed, since it evidently consisted of the unchanged initial product plus a slight trace of hydrolysis products of the ozonides. The aqueous layer yielded acetaldehydedimedone (m.p. 139.1°, m.p of a mixed fusion sample was 139.0°) and acetone oxime (m.p. 58°). No other aldehydes or ketones were found. This indicates that the tested mixture contained 2-methylbutene-2. The presence of appreciable quantities of unsaturated hydrocarbons with a tertiary carbon atom attached to the double atom in the product subjected to ozonidation indicates that the mixture contained from 87.5 to 95.0% 2-methylbutene-2.

2. Ozonidation of a mixture of the 56-57° fraction (Run 31) and the 55.5 - 56.5° fractions (Runs 25 and 26), totaling 0.8 g. Ozonidation lasted 1 hour. Formaldehyde was found in the hydrolysis products of the ozonides (melting point of the formaldehydedimedone 189-190°). A sample mixed with pure formaldehydedimedone had a m.p. of 189.5°. Quantitative determination of the formaldehyde via the dimedone gave the formaldehyde yield as 75.8%.

The boiling point of the oily layer, determined in a capillary, was 92.5°, which is close to the boiling point of methyl isopropyl ketone (93°). The

oily layer actually exhibited a positive reaction for the methyl ketone (iodoform test). The ozonidation products thus contained formaldehyde and methyl isopropyl ketone. The formation of these products is evidence of the presence of 2,3-dimethylbutene-1 in the mixture.

3. Ozonidation of a mixture of the 73-74° fraction (Run 31), the 72-75° fractions (Runs 25 and 26), and the 70-75° fractions (Runs 23 and 24), totaling 1.4 g in all. Ozonidation lasted 1.5 hours. Acetone was found in the aqueous layer (the acetoneoxime had a m.p. of 59-60° after triple recrystallization from methanol, while a mixed fusion sample had a m.p. of 59°). The acetone was determined quantitatively with hydroxylamine hydrochloride, the acetone yield being 44.5% of the theoretical. No other aldehydes or ketones were found. The presence of acetone in the hydrolysis products indicated that the original product contained 2,3-dimethylbutene-2.

4. Ozonidation of the 77.5 - 79.0° fraction (Run 31), totaling 1.6 g. Ozonidation lasted 1.5 hrs. Pinacolin was identified in the oily layer as the oxime, with a m.p. of 73-74° (a mixed fusion sample had a m.p. of 74°), while the m.p. of the semicarbazone was 156.5 - 157° (a mixed fusion sample had a m.p. of 156.5 - 157°). The pinacolin yield was 30.1% of the theoretical. Formaldehyde was identified in the aqueous layer (the formaldehydedimedone had a m.p. of 190°, and a mixed fusion sample had a m.p. of 189.5 - 190°). The formaldehyde yield was 29.5% based on the weight of the original sample. The presence of formaldehyde and pinacolin in the hydrolysis products of the ozonides indicated that this fraction contained 2,3,3-trimethylbutene-1.

Thus, ozonidation of the specified fractions and analysis of the products of hydrolysis of the ozonides enabled us to demonstrate that the respective catalyze fractions contained 2-methylbutene-2, 2,3-dimethylbutene-1, 2,3-dimethylbutene-2, and 2,3,3-trimethylbutene-1.

Thermal decomposition of 2,3,3-trimethylbutene-1. In order to compare the catalytic cracking of 2,3,3-trimethylbutene-1 with its thermal decomposition we ran a test of the thermal disintegration of 2,3,3-trimethylbutene-1 at 400°.

Table 5 gives the comparative figures on the catalytic and thermal cracking of 2,3,3-trimethylbutene-1. What is characteristic of the thermal disintegration is the absence of the methane and ethane-ethylene fractions in the gas. Propane-propylene and butane-butylene fractions were secured in commensurable quantities. Practically no hydrogen disproportionation occurred in the thermal disintegration.

Catalytic cracking of 3,3-dimethylbutene-1. As we had only a small quantity of the initial product available, we were able to make only a single test of the catalytic cracking of 3,3-dimethylbutene-1. The test conditions and the results secured are shown in Table 3. These figures indicate that the bulk of the gaseous cracking products consists of ethane-ethylene and butane-butylene fractions.

In view of the small amount of catalyze (8.1 g), the latter was fractionated together with the high-boiling fractions of kerosene (200-250°). This enabled us to effect rectification of the product under test with almost no loss. The rectification results are illustrated in Fig. 3, while the figures on the group chemical composition of the various fractions of the catalyze are listed in Table 6. These figures indicate that the initial fraction consisted chiefly of the unchanged 3,3-dimethylbutene-1. The third fraction probably contained 2,3-dimethylbutene-1 (b.p. 55.8°).

Fraction 5 (72-74°) was ozonized, 2.7 g being used. Ozonidation lasted 2.5 hours. Hydrolysis of the ozonides yielded an oily layer as a film, so that

TABLE 5

Catalytic and Thermal Cracking of 2,3,3-Trimethylbutene-1

(Rate of feed: 25 ml per hour; length of run: 1 hour; Temperature: 400°)

Indexes	Thermal cracking	Catalytic cracking
Yield, per cent, by weight:		
Gas	1.1	28.0
Catalyzate	97.0	65.7
Coke, reactor residue, and losses	1.9	6.3
Gas formation, mols per mol of charge	0.022	0.635
Composition of the gaseous products, per cent by volume:		
H ₂	-	0.1
CH ₄	-	6.2
C ₂ H ₄	-	22.6
C ₂ H ₆	-	1.0
C ₃ H ₆	52.2	23.2
C ₃ H ₈	1.5	5.5
iso-C ₄ H ₈	38.8	12.4
n-C ₄ H ₈	3.0	17.3
C ₄ H ₁₀	4.5	11.7
C _n H _{2n}	94.0	75.5
C _n H _{2n} + 2	6.0	25.4
Group chemical composition of the catalyzates, per cent by weight:		
Paraffin and naphthene hydrocarbons	3.3	24.7
Aromatic hydrocarbons	None	None
Unsaturated hydrocarbons:		
Secondary	4.6	6.2
Tertiary	92.1	69.1
Per cent conversion	4.4	85.5

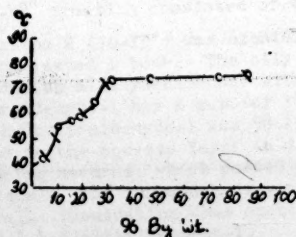


Fig. 3. Rectification curve of the liquid products secured in the catalytic conversions of 3,3-dimethylbutene-1.

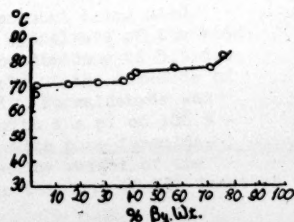


Fig. 4. Rectification curve of the liquid products secured in the catalytic conversions of 4,4-dimethylpentene-1.

TABLE 6

Group Chemical Composition of the Various Fractions of the Catalyzates Secured in the Catalytic Cracking of 3,3-Dimethylbutene-1 and 4,4-Dimethylpentene-1

Fraction No.	Fraction Boiling point	Per cent by weight			
		Paraffin and naphthene hydrocarbons	Aromatic hydrocarbons	Unsaturated hydrocarbons	
				Tertiary	Secondary
Catalytic cracking of 3,3-dimethylbutene-1					
1	40-43°	18.2	None found	7.0	78.8
3	50-60	5.5	ditto	91.0	3.5
5	72-74	26.0	"	72.5	1.5
Catalytic cracking of 4,4-dimethylpetene-1					
2	70-73°	25.2	None found	12.3	62.5
4	76-78	49.5	ditto	21.1	29.4
5	above 78	30.8	9.1	Not determined	

it was not further analyzed. Acetone was identified in the aqueous layer. After double recrystallization from ethyl alcohol the acetone oxime had a m.p. of 58.5 - 59.5°. A sample mixed with the pure oxime of acetone fused at 59 - 59.5°. The acetone yield was 46% of the theoretical. The absence of other aldehydes or ketones is evidence that the bulk of the fraction under test consisted of 2,3-dimethylbutene-2.

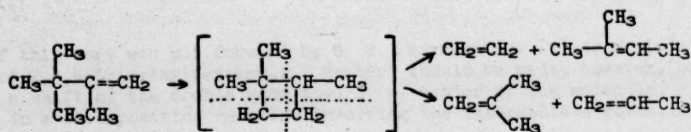
Catalytic cracking of 4,4-dimethylpentene-1. Because of the small quantity of the initial product available, only a single test was made, the results being shown in Table 3. Decomposition of 4,4-dimethylpentene-1 results principally in the formation of propylene and isobutylene, the volume of the propane-propylene fraction (47.1% by volume) corresponding approximately to that of the butane-butylene fraction (49.6% by volume). The fractionation curve of the catalyzate in the column is shown in Fig. 4. The figures on the group chemical composition, especially the data on the percentages of secondary and tertiary unsaturated hydrocarbons in the various catalyzate fractions, indicate that 62.5% of the 70-73° fraction consisted of 4,4-dimethylpentene-1, while 29.4% of the 76-78° fraction consisted of 4,4-dimethylpentene-2.

Fraction 2 (70-73°) was ozonidized, 1.2 g of the product being used. Ozonidation lasted 1 hour. The oily layer formed after hydrolysis of the ozonides yielded an aldehydedimedone with a m.p. of 170° (the dimedone of 3,3-dimethylbutyraldehyde-1 has a m.p. of 167° [19]). The yield of the dimedone of 3,3-dimethylbutyraldehyde-1 was 38.1% of the theoretical. Formaldehyde was identified in the aqueous layer (a dimedone derivative with a m.p. of 188.5 - 189.5° being secured, which passed a mixed fusion test with pure formaldehydedimedone). The formaldehyde yield was 31.0% per cent by weight of the theoretical. Ozonidation thus enabled us to demonstrate that the 70-73° fraction contained 4,4-dimethylpentene-1.

Evaluation of Results

We have utilized the outline of the disintegration of some ethylene hydrocarbons via the intermediate formation of cyclobutane derivatives suggested by S.V. Lebedev and I.A. Vinogradov-Volzhinsky [3] to explain the decomposition of 2,3,3-trimethylbutene-1. We believe that in the presence of an aluminosilicate catalyst 2,3,3-trimethylbutene-1 is decomposed into isobutylene and propylene,

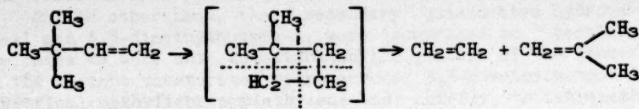
together with ethylene and 2-methylbutene-2, via the intermediate formation of 1,1,2-trimethylcyclobutane:



The gaseous products of the catalytic cracking of 2,3,3-trimethylbutene-1 were found to contain ethylene, propylene, and isobutylene in commensurable quantities, while 2-methylbutene-2 was detected in the catalyzate. Unfortunately analytical difficulties prevented us from establishing the presence of 1,1,2-trimethylcyclobutane experimentally.

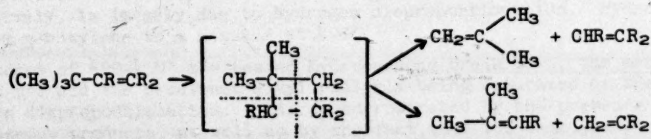
The chief decomposition products are ethylene and 2-methylbutene-2 in the temperature range of 300-350°, with propylene and isobutylene in the 400-450° range.

3,3-Dimethylbutene-1 breaks down to form ethylene and isobutylene. If we consider the disintegration as taking place via a four-membered ring, the reaction may be represented as follows:

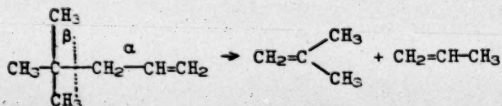


Bearing in mind the assertions we made in our introductory section, we may state that 2,4,4-trimethylpentene-2 disintegrates via the intermediate formation of 1,1,3,3-tetramethylcyclobutane, by analogy with the suggested equations for the decomposition 2,3,3-trimethylbutene-1 and 3,3-dimethylbutene-1. Several authors have commented on the possibility of the intermediate formation of that cyclobutane derivative [2,20].

The data on the catalytic cracking of 2,3,3-trimethylbutene-1, 3,3-dimethylbutene-1, and the 2,4,4-trimethylpentenes, together with the observations of S. V. Lebedev and his associates on the conversions of asymmetrical diphenylethylene [21] and the diamylenes [3] with floridin, support the following outline of the decomposition of unsaturated hydrocarbons of the $(\text{CH}_3)_3\text{C}-\text{CR}=\text{CR}_2$ ($\text{R}=\text{H}, \text{CH}_3$) type via the intermediate formation of cyclobutane derivatives:



The presence of large amounts of propylene and isobutylene in the products of the catalytic cracking of 4,4-dimethylpentene-1 indicate that it is possible for the latter to disintegrate in accordance with the β -bond rule.



A reaction of this sort was put forward by S. N. Obryadchikov [2] to explain the decomposition of 2,4,4-trimethylpentene-1. Mention should be made, however, of the possibility of a shift of the double bond toward the center of the molecule, which would result in a decomposition reaction involving the intermediate formation of a four-membered ring.

It is worthy of note that the conversion of 2,3,3-trimethylbutene-1 into 1,1,2-trimethylcyclobutane obviously involved cyclic tautomerism, analogous to the tautomerism observed in the autocondensation of various glutaric esters [22]. We call this tautomerism hydrocyclotautomerism. It may be assumed that the shift from one tautomeric form to the other depends upon the temperature, this shift not occurring at the temperature at which Lebedev and Kudryavtsev ran their experiments.

The presence of an aluminosilicate results in the isomerization of 2,3,3-trimethylbutene-1, 3,3-dimethylbutene-1, 4,4-dimethylpentene-1, and di-isobutylene, in addition to their disintegration. In the catalytic cracking of di-isobutylene, for instance, the percentage of the "tertiary" unsaturated hydrocarbons decreased. The same state of affairs exists in the catalytic cracking of 2,3,3-trimethylbutene-1. On the other hand, the "secondary" unsaturated hydrocarbons, 4,4-dimethylpentene-1 and 3,3-dimethylbutene-1, were isomerized to "tertiary" compounds. In some cases we were able to establish the pattern of the isomeric transformations of the various unsaturated hydrocarbons: 3,3-dimethylbutene-1 was isomerized to asymmetrical methylisopropylethylene and, chiefly, to tetramethylethylene. This chain isomerism may take place, we believe, via the intermediate formation of a three-membered ring compound. The resultant 2,3-dimethylbutene-1 is apparently isomerized into 2,3-dimethylbutene-2, the double bond being shifted farther into the interior of the molecule. We observed a similar isomerization in the catalytic cracking of 4,4-dimethylpentene-1, which was isomerized to 4,4-dimethylpentene-2.

As we have already said, the catalytic cracking of unsaturated hydrocarbons is accompanied by a hydrogen disproportionation [23]. This is indicated by the drop in the percentage of unsaturated hydrocarbons in the catalyzate below the figure for the initial product. In the temperature range we investigated, the optimum conditions for the disproportionation of hydrogen are obtained at 400-450° for a volumetric rate of raw-material feed of 0.5 volumes per catalyst volume per hour. The hydrogenation of isobutylene and of the *n*-butylenes into isobutane and *n*-butane, respectively, is largely due to hydrogen disproportionation. Hydrogenation of isobutylene and *n*-butylene is a maximum at 400°.

At temperatures of 400-450° the tested hydrocarbons break down, the methyl group being split off and the resultant alkyl radicals being saturated as the result of hydrogen disproportionation. This is corroborated by the presence of methane in the gaseous products, as well as by the fact that the catalyzate secured in the catalytic cracking of 2,3,3-trimethylbutene-1 was found to contain 2,3-dimethylbutene-1 and 2,3-dimethylbutene-2.

In addition to the decomposition, isomerization, and hydrogen disproportionation reactions, the aluminosilicate also causes polymerization of the initial hydrocarbons as well as of the products of the latter's conversions. The polymerization reactions are especially prominent in the 300-350° range, becoming much less

important as the temperature is raised.

At temperatures of 400-450° a small quantity of aromatic hydrocarbons was found in the high-boiling fractions of the catalyzates. We were unable to identify these aromatic hydrocarbons owing to the minute size of these fractions and the small percentage of aromatics contained in them. It is possible for the aromatic hydrocarbons to be formed by the isomerization of the original alkenes to alkenes with six carbon atoms in the chain, followed by their aromatization, or from the cracking products. The latter assumption seems more likely to us.

In conclusion we wish to recall the statement made by C. V. Lebedev [24], to the effect that research on the depolymerization of olefin hydrocarbons was of interest in connection with polymerization processes. In this respect, the conversions we have investigated justify the endeavors of numerous researchers to secure 2,3,3-trimethylbutene-1 from low-molecular unsaturated hydrocarbons. The production of 2,3,3-trimethylbutene-1 from ethylene and 2-methylbutene-2 or isobutylene is thermodynamically feasible. Thermodynamically speaking, these processes may be carried out at high pressures and fairly high temperatures (Fig. 5). The temperatures and pressures must be properly correlated to eliminate competing reactions (polymerization and the like).

SUMMARY

1. The catalytic conversions of 3,3-dimethylbutene-1, 4,4-dimethylpentene-1, and 2,3,3-trimethylbutene-1 with an aluminosilicate catalyst at temperatures of 300-450° and at a volumetric rate of 0.5 liter per liter of catalyst per hour have been investigated for the first time, it being found that the principal conversions occurring were: disintegration, hydrogen disproportionation, polymerization, isomerization, and the formation of coke.

2. The decomposition of 3,3-dimethylbutene-1, 2,3,3-trimethylbutene-1, and (most likely) 2,4,4-trimethylpentene-2, i.e. hydrocarbons of the $(CH_3)_3C-CR=CR_2$ type (where $R = H$ or CH_3), is due to the intermediate formation of four-membered ring compounds in accordance with the outline suggested by S. V. Lebedev to explain the depolymerization of the decenes.

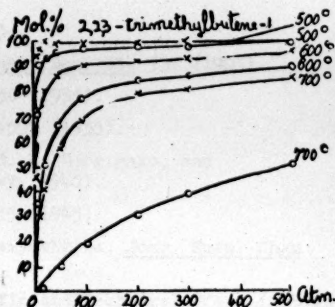


Fig. 5. Variation of the equilibrium percentage conversion with temperature and pressure for the reaction ethylene + 2-methylbutene-2 $\rightarrow$ 2,3,3-trimethylbutene-1 (o) and for the reaction propylene + isobutylene $\rightarrow$ 2,3,3-trimethylbutene-1 (x) (temperatures are given on the absolute scale).

LITERATURE CITED

- [1] R. D. Obolentsev, *J. Appl. Chem.* **22**, 157 (1949).
- [2] S. N. Obryadchikov, *The mechanism and chemism of catalytic cracking*. State Fuel Technology Press, Moscow-Leningrad (1946).
- [3] S. V. Lebedev and I. A. Vinogradov-Volzhiński, *Jour. Russ. Chem. Soc.* **60**, 411 (1928).

- [4] S. V. Lebedev and N. A. Kudryavtsev, J. Gen. Chem. **5**, 1895 (1935).
- [5] Physico-Chemical constants of individual hydrocarbons, Part 1, ed. M. D. Tilicheyev. State Fuel Technology Press (1945).
- [6] Ibid., Pt. II, ed. M. D. Tilicheyev. State Fuel Technology Press (1947).
- [7] Methods of industrial analysis applicable to the synthesis of hydrocarbon fuels. State Fuel Technology Press (1941).
- [8] B. A. Kazansky, M. I. Rozengart, and O. P. Solovova, Izv. USSR Acad. Sci. Div. Chem. Sci. 1941, 97.
- [9] G. D. Galpern and E. V. Vinogradova, Chem. Solid Fuels **4**, 384 (1937).
- [10] B. V. Ioffe, Dokl. USSR Acad. Sci. **53**, 437 (1946).
- [11] B. L. Moldavsky and V. Zharkova, J. Gen. Chem. **14**, 4-5, 359 (1944).
- [12] V. M. Tolstopyatov, Jour. Russ. Chem. Soc. **62**, 1813 (1930).
- [13] R. D. Obolentsev. Physical constants of the constituents of light motor fuels. State Fuel Technology Press (1943).
- [14] L. A. Chugayev, Ber., **32**, 3332 (1899).
- [15] V. Fomin and N. Sokhansky, Ber., **46**, 244 (1913).
- [16] E. E. Vagner and V. O. Brikner, Jour. Russ. Chem. Soc. **35**, 537 (1903).
- [17] J. Schurman and C. Boord, J. Am. Soc., **55**, 4930 (1933).
- [18] F. Whitmore and A. Homeyer, J. Am. Soc., **55**, 4555 (1933).
- [19] B. A. Kazansky, A. L. Liberman, A. F. Plato, S. R. Sergienko, and Academician N. D. Zelinsky, Dokl. USSR Acad. Sci. **27**, 447 (1940).
- [20] J. Kinley and D. Stevens, J. Am. Soc., **67**, 1455 (1945).
- [21] S. V. Lebedev, I. A. Andreyevsky, and A. A. Matyushkina, Jour. Russ. Chem. Soc. **54**, 223 (1922).
- [22] D. V. Beker. Tautomerism, 144. United Scientific and Technical Press (1937).
- [23] A. A. Mikhnovskaya and A. V. Frost, Dokl. USSR Acad. Sci. **37**, 252 (1942).
- [24] S. V. Lebedev, Jour. Russ. Chem. Soc. **45**, 1249 (1913).

Received November 4, 1949.

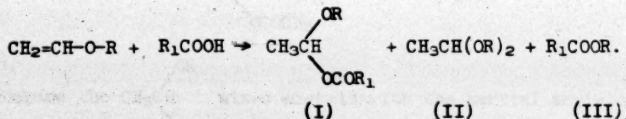
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The N. G. Chernyshevsky State University
of Saratov

THE CONVERSIONS OF VINYL ETHERS

VI. THE CHEMICAL PROPERTIES OF PARTIAL ACYLALES OF THE $\text{CH}_3\text{CH} \begin{matrix} \text{OR} \\ \text{OCOR}_1 \end{matrix}$ TYPE

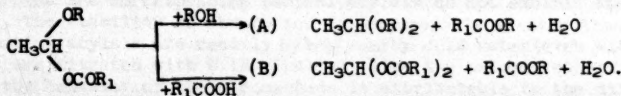
M. F. Shostakovsky and N. A. Gershtein

In our preceding report [1], we found, during a study of the polymerization of vinyl ethers by carboxylic acids, that no polymerization took place, the reaction involving mainly the addition of the carboxylic acids to form partial acyals. At the same time the respective symmetrical acetals and esters were formed:



It was suggested that the formation of products (II) and (III) is due to conversions of the partial acylal (I) under the prevailing reaction conditions.

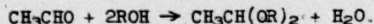
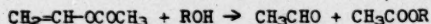
In the present paper we have made a study of the conversions of partial acyals by similar alcohols and acids, as follows



Our supposition has been borne out in the main. In Case (A) it is fairly easy to substitute an acyl group for the alkoxy one, and we were able to recover all the products represented in the above reaction. In Case (B) the replacement of the alkoxy group by an acyl one required more severe conditions, and we did not find the expected complete acylal $\text{CH}_3\text{CH}(\text{OCOR}_1)_2$. We are inclined to attribute our failure in Case (B) to disintegration of the complete acylal, caused by the water evolved during the process. It is not impossible that adding dehydrating agents, such as anhydrides of the respective acids or others that possess neutral or alkaline properties, would be successful.

Croxall, Glavis, and Neher [2] made a study of the reaction involved in the addition of alcohols to vinyl acetate, using a combination catalyst consisting of a coordination compound of the BF_3 with esters, alcohols, or organic acids and HgO in concentrated sulfuric acid. They secured symmetrical acetals and acetic acid as the result of the reaction. They represented the reaction involved as follows: $\text{CH}_2=\text{CHOCOCH}_3 + 2\text{ROH} \rightarrow \text{CH}_3\text{CH}(\text{OR})_2 + \text{CH}_3\text{COOH}$. Hoffman [3] secured an ester of the glycol $\text{HOCH}_2-\text{CH}_2\text{OCOR}$ from vinyl acetate and ethylene glycol by heating equimolar quantities of the latter with mercuric phosphate as a catalyst. Hermann

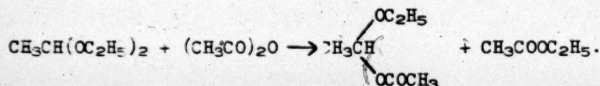
[4] pictures this reaction occurring via an intermediate alcoholysis stage:



The above-mentioned authors [2] also succeeded in isolating α -ethoxyethyl acetate by employing a vinyl acetate:alcohol ratio that approached the equimolar and making sure that their reagents were absolutely anhydrous. The authors suggest that α -ethoxy esters are intermediate products in the reaction involved in synthesizing acetals from vinyl acetate.

This bears out our results regarding the re-esterification of partial acylals by alcohols (A).

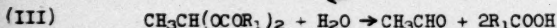
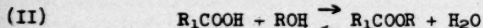
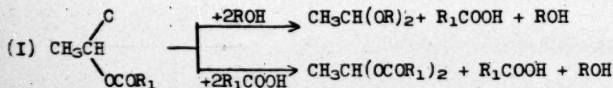
As for our conclusions regarding the re-esterification reaction of partial acylals by carboxylic acids (B), it, too, is supported by the formation of α -ethoxyethyl acetate when diethyl acetate is heated with acetic anhydride [5]:



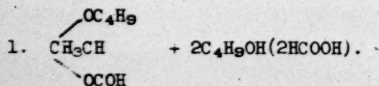
When we compare the $\text{CH}_3\text{CH} \begin{array}{l} \nearrow \text{OR} \\ \searrow \text{OR}_1 \end{array}$ mixed acetals with the partial acylals

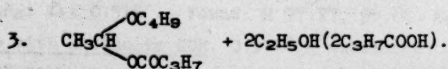
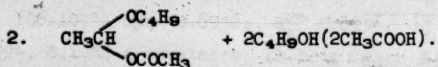
$\text{CH}_3\text{CH} \begin{array}{l} \nearrow \text{OR} \\ \searrow \text{OCOR}_1 \end{array}$ possessing the same acetal grouping, we find that their chemical

behavior differs considerably. Mixed acetals are readily disproportionated into the respective symmetrical acetals when distilled, as we have reported previously [6], whereas the corresponding partial acylals do not exhibit these properties. Still, the stability of the former is incomparably greater than that of the latter. Partial acylals are readily hydrolyzed by cold water (even with no catalyst present), are titrated with 0.1N alkalis, like the halogen ethers, etc. The difference in the behavior of these compounds is attributable to the difference between the C-OR and C-OCOR₁ bonds. Whereas the C-OR bond is almost covalent, the C-OCOR₁ bond is closer to an ionic one. It seems to us that these reactions take place as follows:



In the present paper we have made a study of the re-esterification of partial acylals, using the following examples:





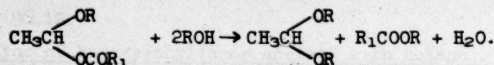
In this research we have isolated and fully identified the following compounds: diethyl and dibutylacetals, butyl formate, butyl acetate, and ethyl butyrate.

Simple hydrolysis reactions were employed to prove the composition and structure of the resultant substances: 1) hydrolysis of the acylals and acetals, with quantitative determination of acetaldehyde by means of sodium bisulfite; 2) hydrolysis, with titration of the resulting acid by an alkali solution; and 3) hydrolysis of the esters with alcoholic KOH.

EXPERIMENTAL

A. Re-esterification of Partial Acylals by Alcohols.

I. Reaction of butoxyethylidene formate and butanol. The quantities of the ingredients used in the reaction corresponded to the following equation stoichiometrically:



A mixture of 23.4 g (0.16 mol) of butoxyethylidene formate and 23.5 g (0.32 mol) of butanol was heated in a sealed ampoule over a boiling water bath for 10 hours. No pressure was found within the ampoule when it was opened. This yielded 46.7 g of a colorless, transparent, acid liquid.

Fractionation in a current of nitrogen: Fraction I: b.p. 38-98° (bulk at 95-98°), 4.8 g, n_D^{18} 1.3912; Fraction II: b.p. 29.5 - 44° at 37 mm (bulk at 38-44°), 17.3 g, n_D^{18} 1.3920; Fraction III: b.p. 45-59° at 37 mm (bulk at 55.5 - 59.5°), 7.7 g, n_D^{18} 1.3920; Fraction IV: b.p. 60-99.5° at 37 mm (bulk at 98-98.5°), 14.7 g, n_D^{18} 1.4090; 1.0 g recovered in the trap. Total: 45.5 g (97%).

The contents of the trap were dissolved in water in a 300-ml measuring flask and then analyzed.

Hydrolysis and determination of the percentage of acetaldehyde. 10 ml of solution: 2.6 ml of 0.1N I_2 ($K = 1.009$). 0.3463 g CH_3CHO found in 300 ml.

Hydrolysis and determination of the percentage of acid. 10 ml of solution: 4.1 ml of 0.1N NaOH ($K = 0.909$). 0.514 HCOOH found in 300 ml.

These figures indicate that the bulk of the contents of the trap consisted of acetaldehyde and formic acid (86.03%).

Fractions I, II, and III, whose refractive indexes were rather similar, could be assumed to contain butyl formate, butanol, and formic acid. The products were processed as follows to recover the individual substances: all three fractions were diluted with sulfuric ether, placed in a separatory funnel, and treated several times with water. The ether solution was desiccated with freshly calcined Na_2SO_4 ; fractionation of the solution then yielded 10.7 g

(65.45%) of pure butyl formate: with the following constants:

B.p. 106-107°; d_4^{20} 0.8952; d_4^{20} 0.8936; n_D^{20} 1.3916; MR_D 27.12;

calc. 26.994. 0.1282 g substance; 12.32 g C_6H_6 ; Δt 0.546°. 0.1268 g substance:

13.04 g C_6H_6 ; Δt 0.515°. Found: M 97.77, 96.86. $C_5H_{10}O_2$. Calculated M 102.

Hydrolysis with alcoholic KOH. 0.1318 g substance: 12.58 g 0.1 N HCl ($K = 1.016$).

Found %: 98.91

We also secured 6.7 g of a substance with a b.p. of 115-117°; n_D^{20} 1.3990, which are the constants for butanol.

Fraction IV was treated in ether solution with metallic sodium, yielding 12.5 g of butyl acetate, with a b.p. of 185-197° (44.82% of the theoretically computed quantity).

d_4^{20} 0.8330; d_4^{20} 0.8315; n_D^{20} 1.4090; MR_D 51.73; calc. 51.66.

0.1555 g substance; 15.50 g C_6H_6 ; Δt 0.3065°. 0.2990 g substance; 15.50 g

C_6H_6 ; Δt 0.5850°.

Found: M 157.9, 169.3 $C_{10}H_{22}O_2$. Calculated: M 174.

Hydrolysis by 2% sulfuric acid, with determination of the percentage of the acetal by means of sodium bisulfite. 0.1056 g substance: 11.85 ml 0.1 N I_2 ($K = 0.9899$). 0.1017 g substance: 11.35 ml 0.1 N I_2 ($K = 0.9899$).

Found %: 96.73, 96.12.

II. Reaction of butoxyethylidene acetate with butanol. The experimental conditions employed were the same as those for Experiment I. A mixture of 21 g (0.125 mol) of butoxyethylidene acetate and 18.5 g (0.25 mol) of butanol was placed in a sealed ampoule and heated over a water bath for 10 hours. No pressure was detected when the ampoule was opened.

Fractionation in a current of anhydrous nitrogen: Fraction I: B.p. 34-52° at 35 mm (bulk at 50-52°); Fraction II: b.p. 52-53° at 35 mm, n_D^{20} 1.3965; (Combined weight of Fractions I and II = 21.63 g; Fraction III: b.p. 60-98° at 35 mm; n_D^{20} 1.4105; weight 15.87 g. Residue left in the flask: 0.84 g 0.43 g collected in the trap. Total: 38.77 g (98.15%).

The trap contents were processed by the sulfite method, yielding 0.218 g of CH_3CHO , and by titration, yielding 0.0463 g of CH_3COOH .

Fractions I and II, consisting of butyl acetate, butanol, and acetic acid, were treated in ether solution with a weak solution of soda and with a concentrated solution of calcium chloride, yielding 9.85 g (67.96% of the theoretical quantity) of butyl acetate, the constants of which were:

B.p. 124.8 - 125.3°; d_4^{20} 0.8815; d_4^{20} 0.8798; n_D^{20} 1.3950; MR_D 31.583; calc. 31.562.

Hydrolysis with alcoholic KOH. 0.0802 g substance: 6.7 ml. 0.1 N. HCl ($K = 1.0161$). Found %: 98.71.

Fraction III was treated with metallic sodium in absolute alcohol, yielding 12.4 g (57.01%) of butyl acetal:

B.p. 184 - 185°; d_4^{20} 0.8332; d_4^{20} 0.8317; n_D^{20} 1.4090; MR_D 51.71; calc. 51.666.

0.1582 g substance; 14.17 g C_6H_6 ; Δt 0.328°. 0.2620 g substance; 14.17 g C_6H_6 ; Δt 0.554°. Found M 174.6, 171.2. $C_{10}H_{22}O_2$. Calculated M 174.

Hydrolysis, with determination of the percentage of acetal via acetaldehyde.
 0.2459 g substance: 27.45 ml. 0.1 N. I_2 ($K = 1.009$). 0.1884 g substance:
 21.45 ml. 0.1 N I_2 ($K = 1.009$). Found %: 97.99, 99.94.

III. Reaction of ethoxyethylidene butyrate with ethyl alcohol. A mixture of 15 g (0.094 mol) of ethoxyethylidene butyrate and 8.63 g (0.18 mol) of ethyl alcohol was sealed into an ampoule and heated to 154-159° for 10 hours over an oil bath. No pressure was detected when the ampoule was opened.

Fractionation in a current of anhydrous nitrogen: Fraction I: B.p. 35-80° (bulk at 78-80°); n_D^{20} 1.3810; Fraction II: b.p. 82-113°; n_D^{20} 1.3790; (weight of Fractions I and II = 12 and 39 g, respectively); Fraction III. 114-122°; n_D^{20} 1.3905, 8.3 g; flask residue: 1.89 g; collected in trap: 0.35 g. Total: 22.93 g (97%).

Fractions I and II, which were mixtures consisting chiefly of ethyl alcohol and diethyl acetal, were diluted with sulfuric ether and treated repeatedly with water and a strong solution of potash, after which they were desiccated with calcined potash. The potash filtrate was treated with metallic sodium to bind the traces of water and ethyl alcohol. Driving off the ether yielded 5.5 g of diethyl acetal (50% of the theoretical quantity).

B.p. 103-104°; d_4^{20} 0.829; d_4^{20} 0.8275; n_D^{20} 1.3818; M_R 33.10; Calc. 33.194.

0.1356 g substance; 18.54 g C_6H_6 : t 0.3275°. Found: M 114.6. $C_8H_{14}O_2$. Calculated: M 118.

Fraction III (b.p. 114-122°) was diluted with sulfuric ether treated with a 1% soda solution, water, and a strong solution of calcium chloride, and desiccated with freshly calcined Na_2SO_4 . Driving off the ether yielded 7.5 g of ethyl butyrate (68.8% of the theoretical quantity).

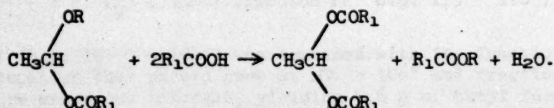
B.p. 117.2-117.8° at 748 mm; 117.5-118° at 760 mm; d_4^{20} 0.8785; d_4^{20} 0.8770; n_D^{20} 1.3930; M_R 31.52; calc. 31.562.

0.1922 g substance; 12.76 g C_6H_6 : Δt 0.707°. 0.1392 g substance; 12.76 g C_6H_6 : Δt 0.500°. Found: M 112.0, 109.5. $C_8H_{12}O_2$. Calculated: M 116.

Hydrolysis with alcoholic KOH. 0.0487 g substance: 4.12 ml. 0.1 N HCl ($K = 1.016$). Found %: 99.70.

B. Reaction of Partial Acylals With Organic Acids

The quantities of the reagents used corresponded to the following equation stoichiometrically:



I Reaction of butoxyethylidene formate with formic acid. A mixture of 20 g of butoxyethylidene formate and 12.6 g of formic acid was sealed into an ampoule and heated for 15 hours over a boiling water bath. The reaction mass turned black. No pressure was found when the ampoule was opened. The reaction products were distilled in an atmosphere of anhydrous nitrogen, the following fractions being collected:

Fraction I: b.p. 90-101° (bulk at 98.5-99°); 25 g; n_D^{20} 1.3825;

Fraction II: b.p. 104-106°; 4.9 g; n_D^{20} 1.3905; flask residue (solid black mass) 1.8 g. Total: 31.7 g (97.24%).

Repeated fractionation of Fraction I failed to yield any pure individual product; it distilled at 97-99.5°. Fraction I might have been expected to contain free HCOOH, butyl formate, and the complete acylal $\text{CH}_3\text{CH}(\text{COOH})_2$. Small samples were hydrolyzed in an effort to determine the composition of this fraction.

Hydrolysis, with determination of the percentage of acylal via acetaldehyde. 0.1875 g substance: 3.1 ml. 0.1 N I_2 ($K = 0.9899$). 0.1532 g substance: 2.15 ml. 0.1 N I_2 ($K = 0.9899$). Found %: $\text{CH}_3\text{CH}(\text{COOH})_2$ 8.93.

Hydrolysis with determinate of the percentage of acid. 0.1798 g substance: 17.6 ml. 0.1 N NaOH. 0.155 g substance: 15.25 ml. 0.1 N NaOH ($K = 1.039$). Found %: HCOOH 46.80, 47.04 (av. 46.92).

On the assumption that titration with alkali in the cold might not hydrolyze the expected ester, (HCOOC_4H_9), the alkali hydrolysis was effected as follows. An excess of a 0.1 N NaOH solution was added to the test sample, a blank test being run with the same quantity of alkali. A weighed sample of the substance under test was heated for 1.5 hours with 0.1N NaOH in apparatus for determining the saponification numbers of esters, a blank test being run with the same quantity of 0.1N NaOH. The excess NaOH was titrated back with 0.1N HCl.

0.2355 g substance: 30.7 ml. 0.1 N NaOH ($K = 1.039$). Found %: HCOOH 62.39.

The difference between the formic acid found in the cold and that found in the last determination proved to be $62.39 - 46.92 = 15.47\%$, which we attributed to the ester (butyl formate) present in Fraction I.

Summarizing the results of our analysis of Fraction I, we may represent its composition as follows: 1) the complete acylal $\text{CH}_3\text{CH}(\text{COOH})_2$: about 10%; 2) butyl formate (by difference from HCOOH): about 15%; and 3) free formic acid and butanol: about 74.5%.

Further processing to separate the reaction products was effected chemically, to wit: the fraction with a b.p. of 97 - 99.5° was diluted with ether and chilled to 0°, and then treated with calcined potash ground to a powder in order to bind the free formic acid. When no more CO_2 was evolved, the ether layer was decanted, while the remaining paste of HCOOK and K_2CO_3 was washed several times with ether. All the ether extracts were combined with the original ether layer and desiccated with freshly calcined Na_2SO_4 . Driving off the ether from the filtrate and distilling yielded: Fraction I. b.p. 103.5 - 104°; 3 g; n_D^{20} 1.3920; Fraction II b.p. 115 - 118°; 4.7 g; n_D^{20} 1.3985.

Fraction I (b.p. 103.5 - 104°) was combined with the fraction of the previous fractionation that passed over at 104 - 106° and fractionated twice in a current of pure anhydrous nitrogen, yielding 5.6 g of butyl formate:

B.p. 105.5 - 106°; d_4^{20} 0.8914; d_4^{20} 0.8899; n_D^{20} 1.3912; M_R 27.20; calc. 26.944.

0.1173 g substance; 13.0 g C_6H_6 : Δt 0.4825°. 0.2072 g substance; 13.0 g C_6H_6 : Δt 0.8535°. Found: M 95.78, 95.80. $\text{C}_5\text{H}_{10}\text{O}_2$. Calculated M 102.

Hydrolysis with alcoholic KOH. 0.1146 g substance: 10.8 ml. 0.1 N HCl ($K = 1.016$). Found %: HCOOC_4H_9 97.67.

The product secured thus was butyl formate, the yield being 40.08% of the theoretical.

Fraction II (b.p. 115 - 118°) proved to be butanol. The potassium formate was decomposed by an aqueous solution of hydrochloric acid, the formic acid evolved being driven off with steam. All the distillate was placed in a 2000-ml measuring flask, the identity of the HCOOH being proved by titration with 0.1 NaOH and by the calomel method.

II. Reaction of butoxyethylidene acetate with acetic acid. A mixture of 20 g butoxyethylidene acetate and 15 g of acetic acid was sealed into an ampoule and heated for 15 hours over a boiling water bath. Fractionation of the reaction products yielded:

Fraction I: b.p. 117 - 118° at 760 mm; n_D^{20} 1.3780, 12.5 g (83.33%);
Fraction II: b.p. 92 - 92.5° at 34 mm; n_D^{20} 1.4040, 17.6 g (88%).

Titration of Fraction I with alkali. 0.3031 g substance: 54.25 ml 0.1 N NaOH. 0.2096 g substance: 38.05 ml 0.1 N NaOH ($K = 0.909$). Found %: CH_3COOH 97.62, 99.01.

Hydrolysis, with determination of the acylal as acetaldehyde. 0.1485 g substance: 18.0 ml 0.1 N I_2 ($K = 1.009$). 0.0968 g substance: 11.8 ml 0.1 N I_2 ($K = 1.009$). Found %: 97.62, 98.40.

These results indicate that no re-esterification reaction takes place at a temperature in the neighborhood of 100°.

III. Reaction of butoxyethylidene acetate with acetic acid at a higher temperature. A mixture of 30 g of butoxyethylidene acetate and 30 g of acetic acid (a slight excess) was sealed into an ampoule and heated to 150 - 159° for 15 hours over an oil bath. The reaction mass turned into a dark-brown, mobile liquid with the choking odor of butyl acetate.

Fractionation in a current of anhydrous nitrogen: Fraction I: b.p. 36.3 - 41° at 34 mm; 19.87 g; n_D^{20} 1.3668; Fraction II b.p. 41.2 - 45° at 34 mm; 27.20 g; n_D^{20} 1.3850; Fraction III: b.p. 45.2 - 47° at 34 mm; 6.48 g; n_D^{20} 1.3890; flask residue 1.70 g.

These figures indicate that none of the initial partial acylal (b.p. 74 - 75° at 2 mm; n_D^{20} 1.4040) or of the sought for complete acylal (b.p. 168 - 169°; n_D^{20} 1.399) is present.

Refractionation in a current of nitrogen at standard pressure: Fraction I: b.p. 108 - 115°; 7.24 g; n_D^{20} 1.3870; Fraction II b.p. 116 - 120°; 28.84 g; n_D^{20} 1.3830; Fraction III b.p. 120 - 125.6°; 15.97 g; n_D^{20} 1.3850.

All three fractions were only partly soluble in water. The boiling points and refractive indexes indicated that the reaction liquid was a mixture of butanol, acetic acid, and butyl acetate. The fractions were treated as follows to isolate these compounds: Fractions I and II were diluted with ether and repeatedly processed with distilled water in a separatory funnel. The aqueous solutions were collected in a 1000-ml measuring flask (Solution No. 1); the ether solution was desiccated with freshly calcined Na_2SO_4 . Fraction III, treated in the same fashion, yielded 300 ml of an aqueous solution (Solution No. 2); its ether solution was combined with the preceding one.

Analysis of the Aqueous Solutions

Determination of the acetaldehyde content of Solution No. 1. 10 ml of solution: 1.95 ml 0.1 N I_2 ($K = 0.9969$). 10 ml of solution: 2.20 ml 0.1 N I_2 ($K = 0.9969$). Found in 1000 ml of CH_3CHO 0.4551 g (on the average).

Determination of the acetaldehyde content of Solution No.2. 10 ml of solution: 3.3 ml 0.1 N I_2 ($K = 0.9969$). 10 ml of solution: 3.3 ml 0.1 N I_2 ($K = 0.9969$). Found in 300 ml of CH_3CHO 0.2212 g. A total of 0.6763 g of CH_3CHO found in both solutions, equivalent to 2.287 g of $CH_3CH(OCOCCH_3)_2$.

Titration with alkali of the aqueous solutions Nos. 1 and 2. 10 ml of solution: 48.45 ml 0.1 N NaOH ($K = 0.909$). 10 ml of solution 48.80 ml 0.1 N NaOH ($K = 0.909$). Average found in 1000 ml: 26.51 g CH_3COOH . 10 ml solution: 20.7 ml. 0.1 N NaOH ($K = 0.909$). 10 ml solution: 20.8 ml. 0.1 N NaOH ($K = 0.909$). Average found in 300 ml: 3.395 g of CH_3COOH . A total of 29.905 g of CH_3COOH was found in both solutions.

The ether solution yielded 14.97 g of butyl acetate, with the following constants, after the ether had been driven off and the residue distilled twice:

B.p. 125 - 126°; d_{20}^{20} 0.8810; d_4^{20} 0.8794; n_D^{20} 1.3952; MR_D 31.63; calc. 31.562.

0.175 g substance; 13.21 g C_6H_6 : Δt 0.615°. 0.2207 g substance; 13.21 g C_6H_6 : Δt 0.787°. Found: M 110.5, 111.5. $C_6H_{12}O_2$. Calculated: M 116.

Hydrolysis with alcoholic KOH. 0.0809 g substance: 6.76 ml 0.1 N HCl ($K = 1.016$). Found %: $CH_3COOC_4H_9$ 98.46.

IV. Reaction of ethoxyethylidene butyrate with butyric acid. 10 g of ethoxyethylidene butyrate and 11 g of butyric acid were sealed into an ampoule and heated to 170 - 175° for 10 hours over an oil bath. The resultant reaction mass was a highly mobile, yellow liquid, with an apple fragrance.

Fractionation in a current of nitrogen: Fraction I: b.p. 30 - 35°; 0.8 g; Fraction II: b.p. 90 - 129° (with water), 8.9 g; Fraction III: b.p. 130 - 162°; 8.64 g; flask residue: 0.97 g; 0.85 g collected in trap. Total: 20.38 g. Losses: 0.62 g.

The contents of the trap and of the first receiver were dissolved in water and brought up to a volume of 1000 ml, after which they were analyzed.

Hydrolysis with determination of the acylal as acetaldehyde. 10 ml of solution: 1.1 ml 0.1 N I_2 ($K = 0.9969$). 10 ml of solution: 1.15 ml 0.1 N I_2 ($K = 0.9969$). An average of 0.2467 g of CH_3CHO was found in 1000 ml, equivalent to 1.33 g of $CH_3(OCOC_3H_7)_2$.

Hydrolysis with determination of the acylal as acid. 10 ml of solution: 2.25 ml 0.1 N NaOH. 10 ml of solution: 2.20 ml 0.1 N NaOH ($K = 0.909$). An average of 1.78 g of C_3H_7COOH was found in 1000 ml.

Fraction II was processed as in the preceding experiments, repeated fractionation yielding 4.58 g (63%) of ethyl butyrate.

B.p. 118 - 120°; d_{20}^{20} 0.8785; d_4^{20} 0.8770; n_D^{20} 1.3955; MR_D 31.58; calc. 31.562.

0.0801 g substance; 12.75 g C_6H_6 : Δt 0.281°. 0.1397 g substance; 12.75 g C_6H_6 : Δt 0.4955°. Found: M 114.7, 113.4. $C_6H_{12}O_2$. Calculated: M 116.

Hydrolysis with alcoholic KOH. 0.1274 g substance: 10.75 ml 0.1 N HCl ($K = 1.016$). Found %: $C_3H_7COOC_2H_5$ 99.45

These results prove that the partial acylals are re-esterified by analogous acids in the reactions set forth above. Under the prevailing reaction conditions the complete acylals are decomposed by the water evolved.

SUMMARY

1. A study has been made of the reaction of partial acylals with the respective analogous alcohols. It has been shown that this reaction results in the formation of acetals and esters.

2. A study has been made of the reaction of partial acylals with analogous acids, involving the formation of the respective complete acylals and esters. Under these conditions the complete acylals are hydrolyzed.

3. The results are discussed and a mechanism is suggested for these transformations.

LITERATURE CITED

- [1] M. F. Shostakovsky and N. A. Gershtein, J. Gen.Chem. 21, 1452 (1951).¹⁾
- [2] Croxall, Glavis and Neher, J.Am.Soc., 70, 2805 (1948).
- [3] Hoffman, US Patent 2,384,726 (1945).
- [4] Herrmann, German-British Patent 314646 (1929).
- [5] Sillimann, Am. J. of Science, 44, 371 (1917).
- [6] M F. Shostakovsky and N. A. Gershtein, J. Gen.Chem. 16, 937 (1936).
- [7] N. A. Gershtein and M F. Shostakovsky, J.Gen. Chem. 18, 451 (1948).

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Received October 27, 1949.

¹⁾ See Consultants Bureau English translation, p. 1581.

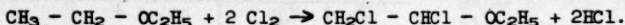
THE SYNTHESIS OF α,β -DICHLOROETHYL ALKYL ETHERS AND THEIR TRANSFORMATIONS

II. THE SYNTHESIS OF α,β -DICHLOROETHYL METHYL α,β - DICHLODIETHYL AND α,β -DICHLRODIETHYL AND ISOPROPYL ETHERS

M. F. Shostakovsky and F. P. Sidelkovskaya

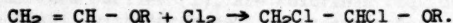
The present paper represents a continuation of our researches [1] on the addition of chlorine to vinyl ethers in order to synthesize α,β -dichloroethyl alkyl ethers with the following general formula:
 $\text{CH}_2\text{Cl}-\text{CHCl}-\text{OR}$.

Ethers of this structure are extremely reactive and may be utilized for the synthesis of all sorts of compounds. For a long time, however, these ethers were substances that were hard to produce and little-known. Suffice it to say that prior to the researches of our laboratory there was only one representative of the α,β -dichloroethyl alkyl ethers mentioned in the literature (α,β -dichlorodiethyl ether). α,β -dichlorodiethyl ether was first synthesized by Lieben [2] by chlorinating diethyl ether:



Up to recently this was the sole known procedure, with a few improvements [3], for the production of alpha, beta-dichlorodiethyl ether; it cannot be utilized, however, in the synthesis of other representatives of the homologous series of alpha, beta-dichloroethyl alkyl ethers

A generally applicable and fairly convenient method of producing alpha, beta-dichloroethyl alkyl ethers is the one based upon the addition of chlorine to vinyl ethers:



In one of our preceding reports [1], we described the addition of chlorine to vinyl butyl and vinyl isoamyl ethers, alpha, beta-dichloroethyl butyl and alpha, beta-dichloroethyl isoamyl ethers being synthesized.

The present paper describes a significant improvement in the method of synthesizing alpha, beta dichloroethyl alkyl ethers described previously [4], which has been applied in the synthesis of alpha, beta-dichlorodiethyl methyl, alpha, beta-dichlorodiethyl, and alpha, beta-dichloroethyl isopropyl ethers.

The distinguishing feature of this new procedure for carrying out the specified reaction is that the process is carried out at a low concentration of the initial vinyl ether for a large part of the time, this being achieved by diluting it with the halogen and with the resulting chlorination products. The reaction rate is maintained constant by regulating the cooling and the rate of chlorine supply. Under these conditions the process is quieter, involving no polymerization, and takes place fast enough, which is of special importance in applying the reaction on a large scale. These conditions were worked out in the reaction involved in adding chlorine to vinyl butyl ether and then applied to several other vinyl ethers.

The characteristics of the synthesized ethers are listed in Table 1.

TABLE 1

Characteristics of Alpha, Beta-Dichloroethyl Alkyl Ethers

Formula	B. p./mm	n_D^{20}	d_4^{20}
$\text{CH}_2\text{Cl}-\text{CHCl}-\text{OCH}_3^1$	24.5-24.7/11	1.4480	1.2377
$\text{CH}_2\text{Cl}-\text{CHCl}-\text{OC}_2\text{H}_5$	42.5-43.5/12	1.4435	1.1879
$\text{CH}_2\text{Cl}-\text{CHCl}-\text{OC}_3\text{H}_7$ -iso ¹	34-34.5/9	1.4430	1.1235

acquaintance with the properties of alpha, beta-dichloroethyl methyl ether and its derivatives led us to conclude, however, that the substance with a b. p. of 137 - 138°, which the author mistook for alpha, beta-dichloroethyl methyl ether, actually was dimethyl chloroacetal $\text{CH}_2\text{Cl}-\text{CH}(\text{OCH}_3)_2$ (b.p. 134°).

In the lower homologs of the vinyl ethers ($\text{R} = \text{CH}_3$, C_2H_5 , and $\text{iso-C}_3\text{H}_7$) the reaction with chlorine is extremely violent and does not stop at the stage in which the dichloro ethers are formed. The latter are further chlorinated, in part, giving rise to the alpha, beta, beta-trichloroethyl alkyl ethers $\text{CHCl}_2-\text{CHCl}-\text{OR}$, depressing the yield of the principal reaction product. This yielded alpha, beta, beta trichloroethyl methyl ether, alpha, beta, beta-trichloroethylethyl ether and alpha, beta, beta trichloroethyl isopropyl ether, the constants of which are tabulated in Table 2.

TABLE 2

Characteristics of Alpha, Beta, Beta-Trichloroethyl Alkyl Ethers

Formula	B. p./mm	n_D^{20}	d_4^{20}
$\text{CHCl}_2-\text{CHCl}-\text{OCH}_3^1$	50.5/9	1.4722	1.4210
$\text{CHCl}_2-\text{CHCl}-\text{OC}_2\text{H}_5$	51-52/5	1.4633	1.3195
$\text{CHCl}_2-\text{CHCl}-\text{OC}_3\text{H}_7$ -iso ¹	63-64/11	1.4640	1.2861

identified by its semicarbazone and its 2,4-dinitrophenylhydrazone.

The alpha, beta-dichloroethyl alkyl ethers synthesized in the present research, like those described earlier [1], are colorless liquids with a penetrating odor, which distill with decomposition at atmospheric pressure. They form tar when heated above 100°, turning into a black, rubberlike mass at first and then into a brittle porous mass when heated to a higher temperature for a long time. Alpha, beta-dichloroethyl alkyl ethers fume in the open air, gradually liberating hydrogen chloride.

The lower members of this series are particularly unstable. Three to four hours after synthesis of the alpha, beta-dichloroethyl methyl, ethyl, and isopropyl ethers, for example, their molecular weights, as determined cryoscopically, are found to have dropped off. This may be due to an increase in the number of molecules in the system, owing to a disintegration reaction. That is why freshly distilled substances must be used in determining the constants of the dichloroethyl alkyl ethers.

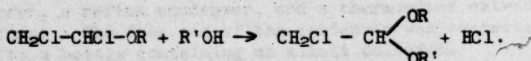
The alpha, beta dichloroethyl alkyl ethers are highly reactive substances. As has been said previously [1], the most interesting property of these

¹ These compounds have been synthesized for the first time.

In 1923 Reichert [5] published a paper in which he mentions the alpha, beta-dichloroethyl methyl ether he had synthesized by chlorinating dimethyl acetal. The only constant he gives for the ether is its boiling point (137 - 138°). Closer

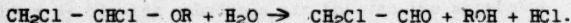
The structure of the trichloroethyl alkyl ethers that contain one chlorine atom at the alpha position and two chlorine atoms at the beta position was demonstrated by hydrolysis, the resultant product being dichloroacetaldehyde,

compounds is the extremely high activity of the alpha chlorine atom. For instance, alpha, beta-dichloroethyl alkyl ethers react vigorously with alcohols and alcoholates, forming acetals of chloroacetaldehyde:



They throw down silver chloride instantaneously from an aqueous solution of silver nitrate. We know from the literature on alpha, beta-dichlorodiethyl ether that a characteristic reaction of this compound, as of other α - and β -halogen ethers [6], is the replacement of the alpha chlorine atom by other groups (R, OCOR, OR, CN, etc. [2,7,8]). A no less interesting property of alpha,beta-dichloroethyl alkyl ethers is the increased activity of the β -hydrogen atom in the chlorinated section of the molecule [1,9]. When reacted with tertiary aliphatic-aromatic amines, for example, they split off hydrogen chloride, forming beta-chlorovinyl alkyl ethers.

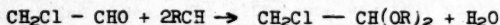
Another striking property of alpha,beta-dichloroethyl alkyl ethers is the readiness with which they are saponified by water at room temperature:



The hydrolysis products are chloroacetaldehyde, hydrogen chloride and an alcohol. When shaken for a long time with water, the bulk of the product turns into a chloroacetal, probably as the result of the following secondary reaction:



or



The hydrogen chloride evolved may be titrated back with alkali or silver nitrate. That is why titration of a sample of alpha,beta-dichloroethyl alkyl ethers (in aqueous medium) with the reagents specified is a convenient analytical method of determining them; we have utilized it extensively in determining the structure and composition of the products synthesized.

The facility with which alpha,beta-dichloroethyl alkyl ethers are hydrolyzed, forming chloroacetaldehyde, is also demonstrated by the fact that they exhibit certain aldehyde reactions with aqueous aldehyde reagents. With Schiff's reagent, for example, they produce a pink color, rapidly changing to violet; they form a crystalline derivative of chloroacetaldehyde when reacted with 2,4-dinitrophenylhydrazine in hydrochloric acid. This ability of alpha,beta-dichloroethyl alkyl ethers to react in an aqueous medium like chloroacetaldehyde has been utilized by several research workers in various condensation reactions in order to synthesize derivatives of furan, pyrrole, pyridine, and 2-aminothiazole [3,10,11].

Like the alpha,beta-dichloroethyl alkyl ethers, the alpha,beta,beta-trichloroethyl alkyl ethers yield crystalline derivatives of dichloroacetaldehyde when processed with aqueous solutions of aldehyde reagents (semicarbazide hydrochloride, 2,4-dinitrophenylhydrazine). When these derivatives are boiled with water, they are converted into the respective glyoxal derivatives.

EXPERIMENTAL

1. Addition of Chlorine to Vinyl Butyl Ether

The reaction was carried out in a three-necked flask, fitted with a mechanical stirrer, a reflux condenser, and a thermometer extending to the bottom of the flask. The free end of the condenser was connected, via a calcium chloride tube, to a bottle containing an alkali solution.

A gentle current of chlorine, dried with sulfuric acid, was passed through 30 g of anhydrous vinyl butyl ether chilled to 0°. Five to seven minutes later the temperature of the reaction mass began to rise quickly, in spite of the external chilling with an ice-salt mixture (-12 to -15°) and vigorous stirring. The temperature of the reaction mass was kept in the 25-30° range by regulating the rate of chlorine supply. After the liquid to be chlorinated had turned greenish-yellow (usually 30 to 40 minutes after the start of the reaction), the rest of the vinyl ether was added to the reaction flask in small batches and the chlorine feed rate was increased. In this stage we were able to keep the temperature at 30°; notwithstanding the very rapid current of chlorine. The end of the reaction was indicated by the appearance of the greenish-yellow color and the cessation of the spontaneous heating up of the reaction mass. The chlorination of 116 g of vinyl butyl ether (1.16 mols) was complete in 2 hours. The excess chlorine was removed by blowing anhydrous air through the apparatus.

The initial fraction yielded the following fractions: I: 54-73° (20 mm), 10 g; II: 73-85° (20 mm), 150 g; III: 85-90° (20 mm), 10 g; tar in residue: 25 g.

Refractionation yielded 140 g of alpha,beta dichloroethyl butyl ether, with a b.p. of 56-59° (7 mm). Yield 71%. The dichloroethyl butyl ether had the following constants after further purification: b.p. 50° (6 mm); d_4^{20} 1.1024; n_D^{20} 1.4473.

2. Addition of Chlorine to Vinyl Methyl Ether

The addition of chlorine to vinyl methyl ether was effected, in the main, under the conditions specified above. The difference was that another gas-supply tube was inserted into the reaction flask to introduce gaseous vinyl methyl ether. The two gases were continuously fed into the system at such a rate as to keep the temperature of the reaction mass from exceeding 25-30° with external chilling (-13°). Complete chlorination of 29 g (half a mol) of vinyl methyl ether required 5 hours. The gain in weight was 29 g. The dissolved chlorine was eliminated by blowing anhydrous air through the mass.

Double fractionation yielded three fractions: I: 30-40° (18 mm), 28 g; II: 40-60° (18 mm), 16 g; III: 60-75° (18 mm), 10 g; and 2 g of tar as the residue.

Fractions I and II yielded 20 g of dichloroethyl methyl ether with a b.p. of 28-30° (15 mm). The yield was 39.3% of the theoretical.

Fractions II and III yielded alpha,beta,beta trichloroethyl methyl ether with a b.p. of 53-56° (11 mm), totalling 17 g. The yield was 20.7% of the theoretical.

Dichloroethyl methyl ether had the following constants after further purification.

B.p. 24.5-24.7° (11 mm); n_D^{20} 1.4480; d_4^{20} 1.2317; M_R 27.94; calc. 27.43

0.1139 g substance; 18.50 g benzene: Δt 0.240°; 0.1830 g substance; 18.00 g benzene: Δt 0.400°; 5.22 mg substance: 5.27 mg CO₂; 2.11 mg H₂O; 6.27 mg substance: 6.31 mg CO₂; 2.58 mg H₂O; 13.270 mg substance: 29.423 mg AgCl; 13.265 mg substance:

29.349 mg AgCl; 0.1322 g substance: 10.17 ml 0.1 N AgNO₃; 0.1623 g substance: 12.45 ml 0.1 N AgNO₃. Found%: C 27.52, 27.45; H 4.52, 4.60; Cl 54.85, 54.75; Cl 27.24, 27.22. M 131.5, 130.3. C₃H₅OC1₂. Calculated %: C 27.88; H 4.68; Cl 54.92; Cl' 27.52 (per chlorine atom); M 128.96.

The alpha,beta,beta-trichloroethyl methyl ether secured in this reaction had the following constants:

B.p. 50.5° (9 mm); n_D²⁰ 1.4722; d₄²⁰ 1.4210; MR_D 32.15; calc. 32.29.

6.223 mg substance; 5.051 mg CO₂; 1.736 mg H₂O; 7.341 mg substance: 5.977 mg CO₂; 2.119 mg H₂O; 78.760 mg substance: 23.000 mg AgCl; 79.602 mg substance: 25.151 mg AgCl; 0.0741 g substance: 4.66 ml 0.1 N NaOH; 1 0.1031 g substance: 6.40 ml 0.1 N NaOH; 0.0741 g substance : 4.55 ml 0.1 N AgNO₃: 0.1031 g substance: 6.25 ml 0.1 N AgNO₃; 0.2010 g substance; 18.10 g benzene: Δt 0.360°; 0.1592 g substance; 18.15 g benzene: Δt 0.288°. Found %: C 22.14, 22.20, H 3.12, 3.23; Cl 64.94, 64.80; equivalent 159, 160.8; Cl 21.77, 21.53; M 158.6, 156.6. C₃H₅OC1₃. Calculated %: C 22.05; H 3.08; Cl 65.10; equivalent 163.41; Cl' 21.70 (per chlorine atom); M 163.41.

Reaction of alpha,beta,beta-trichloroethyl methyl ether with 2,4-dinitrophenylhydrazine. 0.18 g of the trichloroethyl methyl ether was added to a hot solution of 0.2 g of 2,4-dinitrophenylhydrazine dissolved in 5 ml of 10% hydrochloric acid. Bright-orange crystals of the 2,4-dinitrophenylhydrazone of glyoxal: m.p. 314-315° (after recrystallization from alcohol) were observed to form slowly.

3.253 mg substance: 4.733 mg CO₂; 0.805 mg H₂O Found%: C 39.71; H 2.77. C₁₄H₁₀O₆N₂. Calculated %: C 40.18; H 2.41.

3. Addition of Chlorine to Vinyl Ethyl Ether

Chlorine was added to vinyl ethyl ether under the conditions set forth for chlorinating vinyl butyl ether.

A gentle current of chlorine was passed through 50 g of anhydrous vinyl ethyl ether, chilled to +3°. Chlorination of this batch was complete within 2 hours, after which another 139 g of vinyl ethyl ether was added a little at a time, while the chlorine supply was speeded up. The temperature of the reaction mass did not exceed 40°; the 189 g (2.6 mols) of vinyl ethyl ether was chlorinated in 5 hours. The gain in weight totalled 192 g. The excess chlorine was eliminated by blowing anhydrous air through the mass. Double fractionation yielded the following fractions: I: 35-46° (25 mm), 20 g; II: 46-51° (25 mm), 194 g; III: 53-58° (25 mm), 30 g; IV: 58-80° (25 mm), 40 g; with 30 g of tar in the residue.

Fractions II and III yielded 206 g of dichlorodiethyl ether with a b.p. of 49-51° (25 mm). The yield was 54.1% of the theoretical.

Fractions III and IV yielded 15 g of alpha,beta,beta-trichlorodiethyl ether with a b.p. 49-54° (5 mm). The yield was 3.12% of the theoretical, based on vinyl ethyl ether.

The alpha,beta-dichlorodiethyl ether possessed the following constants after supplementary purification:

B.p. 42.5-43.5° (12 mm); n_D²⁰ 1.4435; d₄²⁰ 1.1870; MR_D 32.71; calc. 32.04.

1) The alpha,beta,beta-trichloroethyl methyl ether was titrated as were the alpha, beta-dichloroethyl alkyl ethers, the sole change being that the sample of trichloroethyl methyl ether was shaken up with water for 30-40 minutes prior to titration.

Figures in the literature: B.p. 140-147°; d^{15}_4 1.174 [3].

0.1376 g substance; 12.25 g benzene: Δt 0.330°; 0.1421 g substance; 15.25 g benzene: Δt 0.345°; 11.081 mg substance: 22.401 mg AgCl; 7.733 mg substance: 15.579 mg AgCl; 0.0910 g substance: 6.33 ml 0.1 N AgNO₃; 0.1081 g substance: 7.53 ml 0.1 N AgNO₃; 0.0910 g substance: 6.29 ml 0.1 N NaOH; 0.1081 g substance: 7.53 ml 0.1 N NaOH. Found %: Cl 50.00, 49.83; Cl 24.68, 24.72 equivalent 144.6, 143.1 M 139.8; 138.1. C₄H₅OCl₂. Calculated %: Cl 49.65; Cl 24.79 (per chlorine atom); equivalent 142.97; M 142.97.

The alpha,beta,beta-trichlorodiethyl ether had the following constants after purification by fractionation:

B.p. 51-52° (5 mm); n^{20}_D 1.4630; d^{20}_4 1.3195. M_R 37.05; calc. 36.91.

0.1249 g substance; 20 g benzene: Δt 0.190°; 0.1652 g substance; 20 g benzene: Δt 0.247°; 11.13 mg substance: 27.021 mg AgCl; 10.009 mg substance; 24.37 mg AgCl; 0.1149 g substance: 6.30 ml 0.1 N NaOH; 6.33 ml 0.1 N AgNO₃; 0.3113 g substance; 17.2 ml 0.1 N NaOH; 17.15 ml 0.1 N AgNO₃. Found %: Cl 60.04, 60.23. Equiv. 182.4, 182.1. Cl¹ 19.45, 19.48; M 168.3, 171.4. C₄H₅OCl₂. Calculated %: Cl 59.95; equiv. 177.43; Cl¹ 19.98 (per chlorine atom); M 177.43.

Hydrolysis of alpha,beta,beta-trichlorodiethyl ether 10 g of trichlorodiethyl ether was agitated for an hour with 50 ml of water (the temperature of the reaction mass rising to 60°), after which the mixture was heated for another hour to 70-80° over a water bath. The aqueous layer was separated, neutralized with barium carbonate, and fractionated, yielding the following fractions: I: 70-85°, 3 g; II: 85-99°, 5 g.

Fraction I probably consisted of ethyl alcohol. Reacting Fraction II with 2,4-dinitrophenylhydrazine in hydrochloric acid yielded the 2,4-dinitrophenylhydrazone of glyoxal with a m.p. of 313-314° (recrystallized from alcohol).

The glyoxal 2,4-dinitrophenylhydrazone was likewise secured by directly mixing 2,4-dinitrophenylhydrazine dissolved in hydrochloric acid with alpha,beta,beta trichlorodiethyl ether. In this case the crystalline derivative was formed much more slowly.

Reaction of alpha,beta,beta-trichlorodiethyl ether with ethyl alcohol:
 $\text{CHCl}_2\text{-CHCl-OC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CHCl}_2\text{-CH(OC}_2\text{H}_5)_2 + \text{HCl}$. 15 g of absolute ethyl alcohol was added to 11 g of α,β,β trichlorodiethyl ether, the temperature first dropping from 19° to 16°, and then rising to 18°. The reaction mass was then set aside to stand overnight. The hydrogen chloride evolved was removed from the system by blowing dry air through it. Fractionation at 57 mm yielded: Fraction I: 30-40°, 13 g; Fraction II: 52-65°, 4 g; n^{20}_D 1.4350; Fraction III: 65°, 3 g; n^{20}_D 1.4365.

Five g of the diethyl acetal of dichloroacetaldehyde was secured from Fractions II and III after they had been washed with water, neutralized with soda and treated with sodium sulfate.

B.p. 63-65° (56 mm); n^{20}_D 1.4360; d^{20}_4 1.1310; M_R 43.22; calc. 42.93. Literature: B.p. 183-184°; d 1.1383 [7].

4. Addition of Chlorine to Vinyl Isopropyl Ether

A gentle current of chlorine was passed through 20 g of chilled vinyl isopro-

¹) Before titration the sample of trichlorodiethyl ether was agitated with water for two hours.

pyl ether. After five minutes had elapsed, the temperature of the reaction mass began to rise rapidly, reaching 45°.

The temperature was kept within the 25-30° range by regulating the chlorine rate and the external chilling. The rest of the process was carried out under the conditions specified above. The chlorination of 70 g (0.88 mol) of vinyl isopropyl ether was complete within 5 hours. Double fractionation yielded the following fractions: I: 20-40° (6 mm), 71 g; II: 40-60° (6 mm), 15 g; III: 75-85° (6 mm), 5 g; with 30 g of tar as the residue.

Fractions I and II yielded 55 g of α,β -dichloroethyl isopropyl ether with b.p. of 42-45° (15 mm). The yield was 43% of the theoretical.

Fractions II and III yielded 17 g of α,β,β -trichloroethyl isopropyl ether with a b.p. of 57-60° (9 mm). The yield was 11% of the theoretical.

The dichloroethyl isopropyl ether possessed the following constants after supplementary purification:

B.p. 34-34.5° (9 mm); n_D^{20} 1.4430; d_4^{20} 1.1235; M_R 37.07; calc. 36.66.

0.1930 g substance; 23.3 g benzene: Δt 0.280°; 0.2331 g substance; 23.3 g benzene Δt 0.340°; 14.586 g substance: 20.561 mg CO₂; 8.232 mg H₂O; 11.407 mg substance: 16.01 mg CO₂; 6.556 mg H₂O; 0.172 mg substance: 16.859 mg AgCl; 7.853 mg substance: 14.322 mg AgCl; 0.2049 g substance: 12.9 ml 0.1 N NaOH; 0.1117 g substance: 7.18 ml 0.1 N NaOH; 0.2049 g substance: 13.42 ml 0.1 N AgNO₃; 0.1117 g substance: 7.05 ml 0.1 N AgNO₃. Found %: C 38.46; 38.28; H 6.33; 6.43; Cl 45.46, 45.08. Equiv. 158.8, 155.3. Cl 22.3, 21.6; M 152.0; 151.4 C₅H₁₀OC1₂. Calculated %: C 38.22; H 6.42; Cl 45.16; Equiv. 156.99; Cl 22.4 (per chlorine atom).

The synthesized α,β,β -trichloroethyl isopropyl ether possessed the following constants:

B.p. 63-64° (11 mm); n_D^{20} 1.4640 d_4^{20} 1.2861; M_R 41.10; calc. 41.53.

0.1135 g substance; 220 g benzene: Δt 0.140°; 0.1462 g substance; 20.7 g benzene: Δt 0.195°; 16.33 mg substance: 36.532 mg AgCl; 18.501 mg substance: 41.314 mg AgCl; 0.4710 g substance: 25.3 ml 0.1 N NaOH; 26.1 ml 0.1 N AgNO₃. Found: M 189.5, 186.2 % Cl 55.33, 55.24; Equiv. 185.6; Cl 19.7. C₅H₉OC1₃. Calculated %: M 191.44; Cl 55.56; equiv. 191.44; Cl 18.01 (per chlorine atom).

Hydrolysis of α,β,β -trichloroethyl isopropyl ether.

10 g of α,β,β -trichloroethyl isopropyl ether was agitated with 50 ml of water for an hour. Then the reaction mass was heated to 70-80° for one hour over a water bath, after which the aqueous layer was separated, neutralized with barium carbonate, and fractionated. The following fractions were collected: I: 70-85°; n_D^{20} 1.3840; II 85-95°; and III 95-98°.

Fraction I was treated with potash and fractionated, yielding 1.5 g of isopropyl alcohol, b.p. 72-83°; n_D^{20} 1.3780.

Fractions II and III yielded a substance with a b.p. of 95-98°, which proved to be dichloroacetaldehyde contaminated with water.

2 g of semicarbazide hydrochloride was dissolved in the minimum amount of water and neutralized with potash. The resulting neutral solution was filtered and added to the substance with the b.p. of 95-98°. Rubbing with a rod resulted

¹) Titration followed a preliminary agitation of the trichloroethyl isopropyl ether with water for 30-40 minutes.

in the formation of minute crystals of dichloroacetaldehyde semicarbazone. The semicarbazone was washed with water and with absolute alcohol and then dried in a vacuum desiccator above sulfuric acid. M.p. 155° (with decomposition).

The dichloroacetaldehyde semicarbazone was converted into the bis-semicarbazone of glyoxal by boiling it in water. The latter compound is insoluble in organic solvents. We used a substance purified by repeated boiling with chloroform, alcohol, and ether for identification: it did not melt even at 270°, but carbonized rapidly at 275-280°.

1.508 mg substance: 0.621 ml N₂ (17°, 756 mm); 2.227 mg substance: 0.924 ml N₂ (17°, 756 mm). Found %: N-48.33, 48.57. C₄H₈O₂N₆. Calculated %: N 48.88.

SUMMARY

1. The method employed in the synthesis of α,β -dichloroethyl butyl ether, described previously, has been improved, the yield being raised to 71% of the theoretical.
2. The α,β -dichloroethyl methyl, α,β -dichlorodiethyl, and α,β -dichloroethyl isopropyl ethers have been synthesized by adding chlorine to the vinyl ethers.
3. It has been shown that when chlorine is added to vinyl methyl, vinyl ethyl, and vinyl isopropyl ethers, the process does not stop with the formation of α,β -dichloroethyl alkyl ethers, but chlorination goes further, α,β,β -trichloroethyl alkyl ethers being formed. The latter were isolated and described, and their structure proved.
4. It has been shown that α,β -dichloroethyl alkyl ethers are hydrolyzed extremely easily by water, yielding chloroacetaldehyde, alcohol, and hydrogen chloride.
5. A method has been worked out for making analytical determinations of α,β -dichloroethyl alkyl ethers by titrating them with silver nitrate or caustic soda.
6. α,β,β -trichloroethyl alkyl ethers are likewise readily hydrolyzed by water, though somewhat more slowly than the α,β -dichloroethyl alkyl ethers.

LITERATURE CITED

- [1] M. F. Shostakovsky, Yu. B. Kagan, and F. P. Sidelkovskaya, J. Gen. Chem. 17, 957 (1947).
- [2] A. Lieben, Ann., III, 121 (1859); Ann., 146, 150 (1868).
- [3] I. Ya. Postovsky, V. I. Khmelevsky, and N. P. Bednyagina, J. Appl. Chem. 17, 65 (1944); A. N. Pudovik, Izv. USSR Acad. Sci., Div. Chem. Sci. 1948, 529.
- [4] M. F. Shostakovsky, J. Gen. Chem. 14, 102-112 (1944); M. F. Shostakovsky and I. F. Bogdanov, J. Appl. Chem. 15, 249 (1942).
- [5] J. Reichert, J. Bailly, J. Nieuwland, J. Am. Chem. Soc., 45, 155 (1923).
- [6] A. E. Favorsky and M. N. Shchukina, J. Gen. Chem. 15, 385 (1943); M. F. Shostakovsky and A. V. Bogdanova, J. Gen. Chem. 17, 567 (1947).
- [7] A. Bauer, Ann., 134, 175 (1865).
- [8] J. Hauben, E. Pfankuch, Ber., 59, 2397 (1926).
- [9] M. F. Shostakovsky and F. P. Sidelkovskaya, J. Gen. Chem. 20, 620 (1950).¹⁾
- [10] T. Reichstein, H. Zschokke, Helv. Chim. Acta, 15, 263 (1932).
- [11] E. Benary, Ber., 44, 493 (1911).

Received October 15, 1949.

1) C.B. translation, page. p. 655.

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THE POLYMERIZATION OF OLEIC ACID AND ITS METHYL ESTER WITH MOLECULAR
COMPOUNDS OF BORON FLUORIDE AND THE PHOSPHORIC ACIDS

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Several research projects have been carried out recently on the synthesis and investigation of molecular compounds of boron fluoride and the phosphoric acids, which are active catalysts of the polymerization and alkylation of low-molecular alkenes [1]. Of all known polymerization catalysts these are the most active. Deposited on activated charcoal, they polymerize ethene, propene, and the *n*-butenes in the gas phase at atmospheric pressure and 100°, though no polymerization takes place under these conditions when other catalysts are employed. The high catalytic activity of molecular compounds of boron fluoride with the phosphoric acids might lead one to suppose that these compounds would bring about the polymerization of other unsaturated compounds that are hard to polymerize, such as oleic acid. The polymerization of oleic acid and of its esters is of interest for the production of additions to oils, in the first place, and secondly, for the synthesis of polybasic acids, which may be used as raw materials for the synthesis of alkyl resins [2].

Not much information is available on the polymerization of oleic acid by heat and catalysts. All the available papers date from the period in which catalytic reactions and the number of catalysts employed were developing rapidly. A paper was published in 1922 on the polymerization of oleic acid by a silent electric discharge [3], resulting in the formation of highly viscous unsaturated polymers. We also have a paper on the feasibility of polymerizing oleic acid with hydrogen fluoride [4]. The literature likewise cites figures on the polymerization of oleic acid with chlorides of various metals: SnCl_4 , AlCl_3 , SbCl_3 , and BiCl_3 [5], though only the catalytic action of SnCl_4 has been investigated in detail. The polymerization of oleic acid with SnCl_4 yielded viscous polymers, their molecular weight depending upon the amount of catalyst used and the reaction temperature; raising the temperature of the reaction from 20° to 100° and increasing the percentage of catalyst from 5% to 20% caused the molecular weight to rise from 282 to 1600. The polymerization products were a mixture of several polymers, which also contained a small amount of stearic acid. These polymers were decarboxylated, yielding a mixture of high-polymer hydrocarbons. In 1934 a paper was published on the effect of atomic hydrogen upon oleic acid [6]. This reaction, with absolutely no oxygen present, resulted in the formation of stearic acid plus viscous unsaturated polymerization products, which were not investigated.

In 1937 a patent was issued for the polymerization of unsaturated acids containing one double bond, among them oleic acid, with BF_3 [7]. It was reported that polymerizing oleic acid with BF_3 yielded three products of unknown structure; lastly, in 1939, a patent was issued for the synthesis of solids by heating oleic acid to 140-240° with small amounts of Se and Th [8].

In planning our investigation of the polymerization of oleic acid with molecular compounds of BF_3 , we had in mind a study of the polymerization products, if possible. The polymerization catalysts used were molecular compounds of BF_3 with the phosphoric acids, prepared in accordance with the procedure set forth by Topchiyev and Paushtkin [9, 10, 11]. Since the double bonds must be affected when unsaturated compounds are polymerized, the best indexes to this process are the bromine number and the molecular weight. We therefore used the bromine number and the molecular weight of the polymerize as quantitative polymerization indexes in all our experiments.

Tests were made of the polymerization of oleic acid at 100° for 600 minutes, using 5% of the catalyst, in order to compare the catalytic activity of molecular compounds of BF_3 and the phosphoric acids with that of other catalysts. We found that the most active of the molecular compounds of BF_3 and the phosphoric acids was the compound of boron fluoride with orthophosphoric acid, the least active being the compound of boron fluoride with pyrophosphoric acid. This led us to select the compound of boron fluoride with orthophosphoric acid as the preferred catalyst.

The per cent polymerization was calculated in preliminary tests, which indicated that in no case did the molecular weight of the polymer exceed that of the dimer, polymerization taking place as a polymerization of the monoalkenes, i.e., yielding dimers with a single unsaturated bond.

In carrying out the reaction we learned that the bromine number of the polymerization products drops rapidly during the first four hours, while the molecular weight and specific gravity both rise, no appreciable change of the bromine number occurring during the subsequent hours. The bromine numbers were 49.2, 39.4, 38.8, and 38.5, for instance, when the reaction was carried out for 40, 200, 240, 400, and 600 minutes, respectively. On the basis of these results we set the duration of the reaction at 240 minutes. We investigated the polymerization of oleic acid at temperatures ranging from 20° to 100°, the reaction not being explored at higher temperatures because the catalyst was not very stable at temperatures in excess of 100°. In the runs made at 20° the quantity of catalyst used ranged from 1% to 28% of the acid charge. The maximum conversion of the oleic acid was 71-79% at 20°, using 28% of catalyst. The runs made at 60°, with the catalyst ranging from 1.5% to 24%, exhibited bromine numbers that ranged from 56.93 to 34.85, respectively, and molecular weights that ranged from 308 to 529, respectively. In the runs in which 24% of catalyst was used, the acid numbers diminished, indicating that the carboxylic groups were entering into the reaction. It should be noted that when the catalyst totaled more than 15% of the initial raw material, no appreciable change was found to occur in the bromine numbers or molecular weights.

The polymerization of oleic acid is more thoroughgoing at 100°, as is indicated by the change in the bromine numbers from 28.18 to 42.15 and in the molecular weights from 558 to 430. The polymers were found to contain negligible amounts of stearic acid.

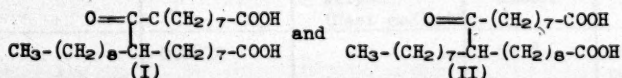
The figure shows the curves representing the variation of the polymer's bromine number with the percentage of catalyst and the reaction temperature. Inspection of the curves shows that they are all alike, regardless of the temperature employed. With a slight increase in the per cent of catalyst, the bromine number decreases and the molecular weight rises at the start of the reaction. A further increase in the amount of catalyst used (above 15%) causes a slight drop in the bromine number for the experiments made at 20° and 60°. In the 100° runs the bromine numbers drop more rapidly than the molecular weights of the polymers rise as the percentage of catalyst is increased. This discrepancy between the decrease in the bromine numbers and the increase in the molecular weights is evidence of the presence of other reactions besides polymerization at this temperature, resulting in the formation of stearic acid. The polymerization products secured in the reaction were unsaturated, their molecular weight not exceeding that of the dimer under all the test conditions employed.

Tests were run of methyl oleate under the same conditions as those used for oleic acid in order to learn the effect of the hydrogen in the carboxylic group upon the polymerization of the acid. Comparison of the catalytic activity of various catalysts in the polymerization of methyl oleate showed that the most

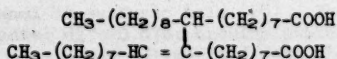
active catalyst again was the molecular compound of BF_3 and orthophosphoric acid under comparable conditions (100° 5% catalyst and a reaction lasting 600 minutes). A study of the effect of the reaction temperature upon the per cent polymerization of methyl oleate indicated that the reaction does not occur at 20° , though its velocity is perceptible at 60° and is best at 100° . Nothing but the dimer of methyl oleate was found in the polymerization of methyl oleate with a molecular compound of BF_3 with orthophosphoric acid. This inference is based upon the fact that the molecular weight of the resultant polymers did not exceed the molecular weight of the dimer. The unpolymerized methyl oleate was separated by virtue of its solubility in absolute methanol, since the polymers of methyl oleate did not dissolve.

It was found impossible to isolate the polymerization products from the polymers of oleic acid, first, because of the inapplicability of vacuum fractionation, and second, because we were unable to discover a selective solvent, as we employed for methyl oleate. In view of the fact that there are numerous references in the literature to the feasibility of isolating polymers of high-molecular unsaturated acids from the polymers of their esters [13, 14] and that various instances of the polymerization of unsaturated acids and their esters demonstrate that the nature of the polymers formed and the method of polymerization remain the same for the acids as well as for their esters [15, 16], we secured the polymers of oleic acid from the polymers of methyl oleate. In doing this we assumed that the resultant dimer of oleic acid may be a mixture of unsaturated dicarboxylic acids, differing solely in the position of their double bonds.

We believed that ozonidation of the mixture of dicarboxylic acids, followed by cleavage of the resultant ozonides, would yield a mixture of various oxidation products, whose identification would fix the position of the double bond. Cleaving the ozonides of the dimer of oleic acid and identifying the cleavage products yielded nonaldehyde, pelargonic acid, and a substance ($\text{C}_{27}\text{H}_{50}\text{O}_5$) that proved to be a mixture of two dicarboxylic keto acids as we had assumed:

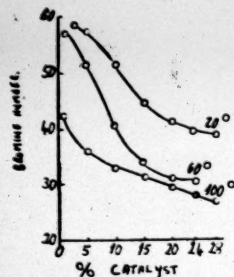


This substance was oxidized to prove that a keto group was present and to determine its position. In view of the possibility that a large number of oxidation products existed, we decided to estimate the position of the keto group by the presence of monobasic acids: caprylic acid for (I) and capric acid for (II). Our investigation of these oxidation products disclosed the presence of a fairly appreciable percentage of caprylic and a negligibly small amount of capric acid, so that we felt we were justified in assuming that the substance with a composition of $\text{C}_{27}\text{H}_{50}\text{O}_5$ consisted of the dicarboxylic keto acid (I). Hence, the bulk of the dimer of oleic acid consisted of an unsaturated dicarboxylic acid, the formula of which was:



EXPERIMENTAL

a) Polymerization of oleic acid. In our experiments we used chemically pure oleic acid that had been first vacuum-distilled at $132-130^\circ$ and 2 mm residual pressure, its constants being found to be: n_D^{20} 0.887, acid number 198.9,



Effect of percentage of catalyst and reaction temperature upon the polymerization of oleic acid.

bromine number 60.1, and n_D^{20} 1.4493. Polymerization was effected in a glass reactor into which the oleic acid was charged together with the measured amount of catalyst. The reaction vessel, fitted with an electrically-driven stirrer, was connected to glass receivers filled with $Ba(OH)_2$ to absorb CO_2 and placed in a thermostat to maintain the required temperature in the reaction zone. We began by running tests on the comparative catalytic activity of various molecular compounds of boron fluoride with the phosphoric acids and of (100%) orthophosphoric acid as catalysts in the polymerization of oleic acid at 100°, the reaction lasting 600 minutes, and the catalyst totaling 5% of the oleic acid charge.

The results of these investigations are tabulated in Table 1.

These figures demonstrate that the molecular compound of orthophosphoric acid with boron fluoride is the most active compound, and it was used as the catalyst in all the subsequent tests. The constants of this compound were as follows: d_4^{20} 1.932; viscosity in poises at 20°: 0.467.

TABLE 1

Catalyst	Sp. gr., d_4^{20}	Molecular weight (Rast method)	Bromine number	Remarks
H_3PO_4 (100%)	0.8872	283	59.8	Does not polymerize
$(C_2H_5)_2O \cdot BF_3$	0.8871	282	59.9	
$H_3PO_4 \cdot BF_3$	0.9261	501	36.8	
$H_4P_2O_7 \cdot 2BF_3$	0.8961	412	45.1	
$HPO_3 \cdot BF_3$	0.9205	485	38.3	

Table 2 gives some of the results of our investigations of the polymerization of oleic acid with the molecular compound of boron fluoride and orthophosphoric acid.

b) Polymerization of methyl oleate. Methyl oleate was prepared by the method described in the literature, consisting of the esterification of oleic acid with absolute methanol in sulfuric acid [16]. The resultant methyl oleate had the following constants: d_4^{20} 0.878; bromine number 54.1, saponification number 191. The methyl oleate was polymerized with the molecular compound of boron fluoride and orthophosphoric acid in the same apparatus and under the same conditions as those used for the acid itself (reaction temperatures: 20, 60, and 100°; length of reaction: 240 minutes). Some of the results of our tests of polymerizing methyl oleate are listed in Table 3.

TABLE 2

Reaction temperature	Per cent catalyst	Length of reaction minutes	Polymer						Calculated per cent polymerization		
			d ₄ ²⁰	Bromine number	Molecular weight	Acid number	Viscosity ₃₅₀	Refractive index at 26°	From the bromine number	From the molecular weight	Mean value
20°	3	240	0.892	58.08	290	201.1	24.61	1.4494	5.7	2.7	4.2
	10	240	0.906	51.43	640	201.0	28.51	1.4502	28.1	27.5	27.8
	20	240	0.917	41.42	455	199.9	39.31	1.4518	61.7	61.3	61.5
60	1.5	240	0.909	56.93	308	199.2	24.9	1.4496	9.7	9.2	9.4
	10	240	0.921	46.64	420	201.2	32.34	1.4511	44.1	48.9	46.5
	20	240	0.931	35.54	505	198.9	45.15	1.4533	81.4	79.0	80.2
	24	240	0.933	34.85	529	168.6	47.97	1.4539	84.3	87.5	86.1
100	3	240	0.899	42.15	430	186.2	38.34	1.4519	58.8	52.4	55.6
	10	240	0.929	35.06	518	168.3	47.15	1.4541	83.3	84.1	83.4
	20	240	0.937	29.63	545	141.2	56.68	1.4549	101.0	93.2	97.1

TABLE 3

Reaction temperature	Per cent catalyst	Length of reaction minutes	Polymer					Calculated per cent polymerization		
			d ₂₀ ⁴	Bromine number	Molecular weight	Viscosity ₃₅₀	Refractive index at 26°	From the bromine number	From the molecular weight	Mean value
60°	5	240	0.889	51.18	323	10.4	1.4426	10.7	9.1	9.9
	10	240	0.896	46.24	371	14.6	1.4457	29.2	25.4	27.3
	20	240	0.909	40.46	448	20.1	1.4488	50.0	51.3	50.6
100	5	240	0.902	44.83	345	15.6	1.4465	34.3	30.1	32.2
	10	240	0.909	41.46	434	19.1	1.4484	47.0	46.6	46.8
	20	240	0.917	36.71	487	23.1	1.4502	64.4	64.6	64.5

c) Isolating the dimer of oleic acid. The dimer of oleic acid was produced by saponifying the dimer of methyl oleate. The procedure used for the recovery of the dimer of methyl oleate involved triple extraction of the polymers of methyl oleate with absolute methanol, followed by saponifying the undissolved polymerization products and eliminating the traces of methanol. The substance left after the CH₃OH had been eliminated had the following physicochemical constants:

Bromine number 27.8; saponification number 190.3
 0.2620 g substance: 0.7436 g CO₂; 0.289 g H₂O. 0.4486 g substance;
 21.0876 g benzene: Δt 1.846°. Found %: C 77.45; H 12.34; M 590.
 (C₁₈H₃₆O₂)₂. Calculated: bromine number 27.8; saponification number 150.3; % C 77.23; % H 12.16; M 594.

The molecular weight and the per cent carbon and hydrogen indicate that this substance is the dimer of methyl oleate, an unsaturated compound (bromine number). The dimer of methyl oleate was saponified with alkali the resulting salt was decomposed with hydrochloric acid, and the organic acid was extracted with diethyl ether, which was driven off at reduced pressure.

The substance secured after the dimer of methyl oleate had been saponified had the following physicochemical constants:

d_4^{20} 0.926; bromine number 29.8; acid number 199
1.1456 g substance; 19.2413 g benzene: Δt 0.070° 0.0814 g substance;
0.4532 g camphor: Δt 12.83°. Found: M 599, 560; $(C_{18}H_{34}O_2)_2$.
Calculated: bromine number 29.9; acid number 198.5; M 564.

d) Ozonating the dimer of oleic acid and identification of the decomposition products The dimer of oleic acid was ozonidated in a carbon tetrachloride solution at -8°. Ozonation lasted 1 hour on the average per gram of the substance. The concentration of the ozone used ranged from 10 to 13%. After the reaction was complete, the solvent was driven off at reduced pressure, analysis of the residual substance giving the following results:

0.2173 g substance: 0.5615 g CO_2 ; 0.2131 g H_2O . 0.2416 g substance:
20.0342 g benzene: Δt 0.102°. Found %: C 70.71; H 10.96; M 603. $C_{36}H_{68}O_7$.
Calculated %: C 70.58; H 11.12; M 612.

The substance synthesized was thus the satisfactorily pure ozonide of the dimer of oleic acid. The ozonides were then cleaved by heating them for 2 hours over a water bath with 4 times their weight of water. After the mixture had cooled, it was treated with a 3% solution of Na_2CO_3 and with ether. The sodium carbonate solution was acidified with hydrochloric acid and extracted with ether; an extremely minute quantity of a substance was found, which proved to be pelargonic acid, as had been assumed from its molecular weight and acid number.

The oily substance recovered after the ether had been removed was fractionated in vacuum, the following definite fractions being collected: capraldehyde (traces) passed over at 23 mm and 65-85°; nonaldehyde at 17 mm and 80-105°; caprylic acid (traces) at 10 mm and 115-130°; pelargonic acid at 10 mm and 130-150°; the residue above 150°/10 mm consisting of high-molecular products. We did not make any investigation of the 65-85°/23 mm fraction, owing to its minute size. It turned fuchsin-sulfurous acid a reddish-purple. The 80-105°/10 mm fraction was refined via a bisulfite compound, after which the semicarbazone was prepared. The semicarbazone had a m.p. of 98.3° after recrystallization from methanol. K. Harries [17] gives 109° as the m.p. of the pure semicarbazone of nonaldehyde. The 115-130°/10 mm fraction, representing caprylic acid, was not identified owing to the infinitesimally minute quantity available. The present authors resolved to confine themselves to a qualitative reaction (heating with o-phthalaldehyde produced a blue color that vanished upon cooling) and an ultimate analysis.

We purified the 115-130°/10 mm fraction via the barium salt and then analyzed it:

Acid number 353.6
0.3017 g substance; 21.131 g benzene: Δt 0.481° 0.1064 g substance;
0.6635 g camphor: Δt 41.72°. Found: M 152, 154. $C_8H_{16}O_2$. Calculated:
M 158; Acid number 354.4

We used the prepared substance to get the lead salt, its melting point being 93° after recrystallization from alcohol. Neave [18] gives 94-95° as the m.p. of the pure lead salt of pelargonic acid.

The residue above 150°/10 mm was a viscous dark substance, which turned sulfurous acid a reddish-purple and proved to be a mixture of high-molecular disintegration products, as we had assumed:

Acid number 281.0

0.856 g substance: 0.4783 g CO₂; 0.1862 g H₂O. 0.1013 g substance;

0.5437 g camphor: Δt 15.9°. Found %: C 69.91; H 10.93; M 468.

C₂₇H₅₀O₅. Calculated %: C 71.36; H 11.01; M 457; Acid number 246.7.

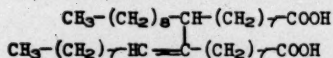
The slight deviations of the measured values of molecular weight, acid number, and per cent carbon and hydrogen from the calculated values may evidently be attributed to the presence of minute traces of high-molecular products, which could only be tricarboxylic acids.

We oxidized the C₂₇H₅₀O₅ substance (150°/10 mm) to prove the presence of a keto group as well as its position, in the belief that the traces of tricarboxylic acids would not interfere, since they do not form oxidation products. The 150°/10 mm fraction was oxidized with potassium permanganate in alkali. In view of the possible presence of a large number of oxidation products, we decided to estimate the position of the keto group by the presence of monocarboxylic acids: caprylic acid for (I) and capric acid for (II). The resultant oxidation products were fractionated in vacuum at 10 mm residual pressure, only two fractions being collected: 121-125° and 159-163°, caprylic and capric acids, respectively.

The 121-125°/10 mm fraction, secured when we distilled the oxidation products, was identified as its lead salt. The melting point of the lead salt was found to be 82°. According to the literature the melting point of the pure lead salt of caprylic acid is 84-85° [18]. We did not analyze the 159-163°/10 mm fraction owing to its minute size.

SUMMARY

1. In a comparison of the catalytic action of various catalysts: H₃PO₄ (100%), (C₂H₅)₂O · BF₃, HPO₃ · BF₃, H₃PO₄ · BF₃ and H₄P₂O₇ · 2BF₃ in the polymerization of oleic acid, the compound of boron fluoride with orthophosphoric acid was found to be the most highly active of the compounds tested.
2. The polymerization of oleic acid and of its ester at various reaction temperatures showed that the per cent conversion rose with the temperature for the acid and for its ester. The per cent polymerization was lower for the methyl oleate than for the acid itself in all the tests (at comparable conditions).
3. Analyses of the resultant polymers (molecular weight, bromine number) indicated that polymerization goes as far as the dimer.
4. The polymerization of methyl oleate yielded the dimer of methyl oleate. Saponifying the latter yielded the dimer of oleic acid, its physicochemical constants and per cent carbon and hydrogen indicating that it is the unsaturated dicarboxylic acid C₅₆H₉₈O₄.
5. The polymerization products of oleic acid have been ozonated for the first time. Ozonation of the dimer of oleic acid yielded the following characteristic derivatives, which were identified: nonaldehyde and pelargonic acid plus a mixture of two dicarboxylic keto acids, with the formula of C₂₇H₅₀O₅.
6. Oxidation of the product with the composition of C₂₇H₅₀O₅ yielded caprylic acid and traces of capric acid, which served as the basis for the conclusion that the bulk of the product consisted of the dicarboxylic keto acid (I), while the dimer of oleic acid consisted of the unsaturated dicarboxylic acid:



LITERATURE CITED

- [1] A.V.Topchiev, Trans. Gubkin Petroleum Institute, Moscow 6, 35 (1947).
- [2] V.S.Kiselev and T.N.Poroptseva, Chem. Ind. 3, 83 (1948).
- [3] E.Eichwald, Z. angew. Chem., 74, 505 (1922).
- [4] K.Fredenhagen, Z. Physik. Chem., A 164, 190 (1933).
- [5] B.Chowdhury. A.Chakrabarty, R. Mazumber, J.Indian Chem. Soc., 12, 446 (1935).
- [6] H.Kroplelin, E.Vogel, Ber., 68, 684 (1935).
- [7] German Patent 463890 (1937).
- [8] U.S. Patent 2,165,540 (1939).
- [9] Ya.M.Paushkin and A.V.Topchiyev, Dokl. USSR Acad. Sci. 13 No.6 (1947).
- [10] A.V.Topchiyev and Ya.M.Paushkin, Chem. Prog. 16 No.6, 667 (1947).
- [11] A.V.Topchiyev and Ya.M.Paushkin, Oil Economy No.6, 59. (1937).
- [12] T.F.Bradley, Ind. Eng. Chem., 32, 695 (1940).
- [13] H.F.Pfang, T.F.Bradley, W.B.Djonson, Ind. Eng. Chem., 32, 804 (1940).
- [14] K.Kinch, Sci. Papers Inst. Phys. Chem. Research (Tokyo), 15, 129 (1931).
- [15] V.Kowan, G.Falkenburg, I.Teter, Ind. Eng. Chem., Anal. Ed., 16, 91 (1944).
- [16] G.Laurent, A. Ch. (2) 65, 299.
- [17] K.Harries, F.Thieme, Ann., 343, 354 (1905).
- [18] G.Neave, Analyst., 37, 399 (1912).

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Received November 14, 1949.

THE VICINAL EFFECT

II. THE ANOMALOUS PROPERTIES OF CARBON FLUORIDES

D. Tischenko

I

Ten years ago the study of the reactivity of aliphatic polychlorides led me to propose the concept of the "vicinal effect" (the effect of proximity) [1].

In that paper I wrote: "The term 'vicinal effect' may be proposed to denote the interaction of two or more polar substituents in an organic molecule. The so-called 'ortho-effect' in aromatic compounds is a special case of the vicinal effect. In the case of negative substituents (in the C - X dipole the valence electron pair is closer to the atom or group X), the vicinal effect boils down to a decrease in the values of the partial dipole moments of the C - X bonds and to an interference with the ionization of the X atoms or groups. In the case of positive substituents (the valence electron pair is closer to C in the C - X dipole), the vicinal effect again results in a decrease of the partial dipole moments of the C - X bonds, but, in contrast to the preceding case, the ionization of the X groups is facilitated. The vicinal effect is most prominently manifested when the polar substituents are closest together, while it practically vanishes when they are separated at the 1,4 positions... The vicinal effect ought to be strongest in atoms having a low atomic number... The vicinal effect is also exhibited by inorganic compounds. We know that salts of a given metal at a lower valency are more highly electrovalent compounds than those of higher valency."

In a later paper [2] we made use of the data published in the literature on the shortening of the bonds between various elements and the halogens as the number of halogen atoms attached to the central atom increased and on the chemical inertness of the saturated polyfluorides and polyfluorochlorides to demonstrate that these facts were in complete agreement with the concept of the vicinal effect and resulted from it. Papers have recently been published that enable us to provide a definite theoretical foundation for the concept of the vicinal effect [3] on the one hand, and to explain the anomalous physico-chemical properties of carbon fluorides, which have remained unexplained hitherto [4] by means of this concept, on the other.

The monograph Molecular Vibrations [3] gives methods for calculating the vibrations of organic molecules with a given Raman or infrared frequency and given form of vibration, together with methods of calculating the constants of the various quasi-elastic forces in the molecules, and compares the computed and observed frequencies, especially for all sorts of halogenomethanes. The excellent agreement of the computed and observed values lead us to conclude that the calculated values of the quasi-elastic forces also correspond to reality. The following potential energy constants (in 10^6 cm^{-2}) are most important in establishing the concept of the vicinal effect: 1) K_x - the quasi-elastic force of the bond C - X; and 2) K_{xx} - the quasi-elastic force of the interaction of the carbon with itself (the return to the state of equilibrium). The values of these constants are given in Tables 1 and 2 (P. 375, V. I. of the monograph).

The data cited (Tables 1 and 2) indicate that the vicinal effect is a real quantity and that it is strongest in elements of low atomic number, as I demonstrated ten years ago. For bromine K_x rises 6% from CXH_3 to CX_4 , 7% for chlorine

TABLE 1

	K_x		
	Br	Cl	F
CH ₄	-	-	-
CXH ₃	4.7	5.8	9.8
CH ₂ H ₂	4.8	5.9	10.7
CX ₃ H	4.9	6.1	10.9
CX ₄	5.0	6.2	12.3

TABLE 2

	K_μ		
	Br	Cl	F
CH ₄	-	-	-
CXH ₃	-	-	-
CX ₂ H ₂	1.32	1.61	1.90
CX ₃ H	1.34	1.62	2.28
CX ₄	1.36	1.63	2.47

and 20% for fluorine; the values of K_μ rise 3, 1.5, and 23% respectively. The increase in K_x for the fluoromethanes, which is far out of line, should be borne in mind in the subsequent discussion of the properties of carbon fluorides.

We know that the vibrational frequency of the bonds, q_x , is, in a first approximation, proportional to the quasi-elastic forces of the bonds. Table 3 gives the values of these frequencies for the halogenomethanes (p. 393, V. I. of the monograph).

TABLE 3

	CCl ₂ Br ₂	CF ₂ Br ₂	CF ₂ Cl ₂	CFC1 ₃	CBrCl ₃	CClBr ₃	CHBr ₃	CHCl ₃	CHF ₃
q_F {		1077 1142	1083 1147	1067					937 1116
q_{Cl} {	720 750		654 877	536 833	710 765	734		668 761	
q_{Br} {	370 670	340 816			418	326 674	539 655		

	CHCl ₂ Br	CHBr ₂ Cl	CHF ₂ Cl	CHCl ₂ F	CHBr ₂ F	CH ₂ Br ₂	CH ₂ Cl ₂	CH ₂ F ₂	CH ₃ Br	CH ₃ Cl	CH ₃ F
q_F {			1088 1120	1066	1064			1078 1136			1049
q_{Cl} {	719 760	750	794	716 794			700 736			732	
q_{Br} {	602	569 659			620 705	576 638			610		

We see from Table 3 that : a) the bond frequency q_x increases as the hydrogen atoms in methane are progressively replaced by halogen atoms; b) that replacing bromine or chlorine by fluorine in mixed halogenomethanes results in an increase in all the q_x frequencies, i.e. a strengthening of all the C - X bonds. These facts compel us to admit that the vicinal effect exists, independent in sign of the nature of the negative substituent, but varying in magnitude with the atomic number of the substituent (in the case of the halogens). In the polyfluorides, the vicinal effect results in the maximum strengthening of all the C - F bonds, these bonds approaching a homopolar state, which must affect all the properties of these compounds in a decisive manner.

II

The research of American chemists during the war is published in the symposium

The Chemistry of Fluorine (Vol. I [4]). The authors of these papers produced various carbon fluorides of different types and investigated their properties, noting numerous pronounced anomalies in the chemical and physical properties of the carbon fluorides but not furnishing any explanation of these anomalies.

We list these anomalies below, henceforth referring to them by number to save space. The figures in parentheses refer to the respective pages of the symposium.

1. Monofluoroalkyls are unstable chemically and sometimes break down spontaneously (18). 2. At 90° carbon fluorides dissolve in alkalis, forming dark-brown solutions (49). 3. Carbon fluorides resist the action of the most powerful chemical agents, even the alkali metals, up to comparatively high temperatures: of the order of 400° (26-27). 4. The dielectric constants of the carbon fluorides C_nF_{2n+2} are lower than those of the hydrocarbons C_nH_{2n+2} ; being 1.76 for C_7F_{16} as against 1.9 for C_7H_{16} ; as hydrogen atoms are introduced into a carbon fluoride, the constant rises rapidly, reaching a maximum (as high as 12.4) and then dropping, (120, 121, 125). 5. The refractive indexes n_D^{20} of C_nF_{2n+2} are 1.24-1.31, while they are 1.36-1.43 for C_nH_{2n+2} . The atomic refraction AR_F is 1.23 for C_nF_{2n+2} , whereas it depends on the number of fluorine atoms in the molecule for the carbon fluorides (57,58):

Number of F atoms.....	1	2	3	4	5	
AR_F	0.95	0.99	1.02	1.08	1.14	1.23

6. Beginning with fluoropentane, the carbon fluorides have lower boiling points than the corresponding hydrocarbons. Their boiling points are exceptionally low, in view of their high molecular weight. They are closer to the inert gases in this respect than any other types of chemical compound (19,26,27). 7. The boiling points of all isomers of fluoropentane are practically identical; the interval for the isomeric hydrocarbons is 21° (54). 8. The boiling points of the hydro-F-heptanes are higher than those of C_7F_{16} or C_7H_{16} (54). 9. The boiling point of perfluoradipodinitile is 232° below the boiling point of adipodinitrile (63° and 295°, respectively, p.201). 10. The temperature coefficient of expansion of the carbon fluorides is twice that of the hydrocarbons (58,59). 11. In view of their high molecular weight, the carbon fluorides exhibit rather high fluidity and low surface tension, apparently constituting liquids with extremely small intermolecular tensile forces (26,27).

As we have said, the American authors merely record these anomalies without explaining them in any way. We shall attempt to supply these explanations. Let us begin with Anomaly 3. As has been stated above, the constant of the quasi-elastic force for the C-F bond increases with the number of fluorine atoms in the molecule (vicinal effect), attaining the value of 12.3 for the carbon fluorides. This figure is far out of line; the only comparable figure for single bond is the constant for the O-H bond, 12.6 (monograph, Vol. I, p.241). Whereas the C-F distance is 1.35 Å, the O-H distance is 0.97 Å; hence the forces binding the C and F atoms together are much greater than those linking the O and H atoms. The constant for the force of the C-F bond in monofluoroalkyls is 9.8, being comparable with the constants of many other single bonds with approximately the same interatomic distances (C-C, C-O, C-H, and C-N). As we know, this bond is a heteropolar one; the marked strengthening of the C-F bond in the carbon fluorides together with their complete inertness chemically, forces us to consider the C-F bond in the carbon fluorides as almost entirely homopolar, with undisplaced electron shells, like the shells of the noble gases, and with zero, or extremely small, values of the partial dipole moments of the C-F bonds, the entire molecule being completely neutral electrically.

Anomaly 1. We have shown previously [2,5] that the most highly "protonized" hydrogen atoms in chloroalkyls are those next to a chlorine atom. This was subsequently established in even more striking form for the fluoroalkyls. Hence, the halogen draws off the valence electron pairs from the closest hydrogen atoms, making them "protonic" and weakening their bond with the carbon atom. Thus, in monofluoroalkyls both the C-F bond and the nearest C-H bond are polar, which ought to make it easier to split out HF by the action of various chemical reagents or protons, thus establishing the instability of the monofluorides.

Anomaly 2. Fluorohydrocarbons with a large number of fluorine atoms in the molecule (such as $C_7F_{15}H$ and $C_7F_{14}H_2$) dissolve in alkalis at 90°. If one atom of fluorine in monofluoroalkyls is able to "protonize" the adjacent hydrogen atoms by attracting their valence electron pairs, the combined action of fifteen fluorine atoms upon a single hydrogen atom must make it almost entirely protonic. Monohydro-F-heptane must be a weak acid, and, as such, it must react with alkalis. Its molecule must be highly asymmetrical electrostatically speaking which ought to be manifested accordingly in its dielectric constant.

Anomaly 4. The dielectric constant is a function of the total dipole moment of the molecule and of the partial dipole moments of the individual bonds. When the molecule, as a whole, is compensated, the partial moments of the bonds predominate, as is the case in C_nH_{2n+2} and C_nF_{2n+2} . We accepted the homopolarity of the C-F bonds in carbon fluorides above. The following conditions do not allow us to consider the C-H bonds in hydrocarbons homopolar: the C-H bonds have a dipole moment of $0.4 \cdot 10^{-18}$. This value is too small, (compared to the dipole moment of the C-F bond, which is $1.6 \cdot 10^{-18}$ in monofluoroalkyls) for the vicinal effect to reduce the partial C-H moments in hydrocarbons to zero. Morton's most recent researches have shown that the higher or lower protonicity of primary, secondary, and tertiary hydrogen atoms may be estimated from their preferential replacement by a sodium atom when the hydrocarbons are reacted with organosodium compounds. As might have been expected, the primary hydrogen atoms turn out to be the most protonic, which is evidence that at least part of the C-H bonds in hydrocarbons are polar. Hydrocarbons react with various chemical reagents at low temperatures, whereas the carbon fluorides do not react with them below 400°, which is further evidence that the C-F bonds in C_nF_{2n+2} are more homopolar than the C-H bonds in C_nH_{2n+2} . If these arguments be adopted as correct, the dielectric constants of the carbon fluorides, substances held together by more highly homopolar bonds, must be lower than the dielectric constants of hydrocarbons, as is actually the case.

As has been shown above, in fluorohydrocarbons that contain a small number of hydrogen atoms, the latter must be highly protonic, while the whole molecule must possess a large dipole moment, resulting in the rise of the dielectric constant. Actually, "the dielectric constant increases almost linearly with an increase in the percentage of hydrogen" (125), though it then falls to the value of the dielectric constant of a saturated hydrocarbon. The fact that these values pass through a maximum is attributable to the circumstance that a small number of fluorine atoms cannot strongly protonize a large number of hydrogen atoms, so that the dipole moments of the C-H bonds progressively drops as the number of fluorine atoms in the molecule is diminished, approaching $0.4 \cdot 10^{-18}$, the "normal" value of the moment for this bond. The decrease of the value of the dielectric constant parallels this drop.

Anomaly 5. Once we admit, as we have done in the foregoing, that the C-H bonds in C_nH_{2n+2} are less homopolar than the C-F bonds in carbon fluorides, then

the fact that the refractive indexes of carbon fluorides are smaller than those of hydrocarbons follows as a consequence.

In the case of negative atoms, the more heteropolar their bonds to atoms of other elements are, the greater their polarizability in the light field. This conclusion may be drawn from a consideration of even the ionic and atomic refractions of the halogens [6] (Table 4).

TABLE 4

	F	Cl	Br	I
R_D of the ion in solution	2.61	9.07	12.67	19.21
R_D of the atom	1.23	5.82	8.69	13.9

Heydweyller does not give AR_D for fluorine, so that we took its value from a handbook. This figure indicates that the polarizability of the ionic bond is much greater than that of a strong homopolar bond and that the transition from a homopolar to a heteropolar bond is accompanied by an increase in polarizability (in negative atoms), and vice versa. The extent to which ionic polarizability exceeds the atomic is 112% for fluorine, 54% for chlorine, 42% for bromine, and 38% for iodine. These figures again underline the exceptional position of fluorine in the halogen series: there is much more "room" in fluorine for the manifestation of the vicinal effect. Hence, these considerations also point to the approach of the C-F bonds in carbon fluorides to a homopolar state, which is characterized by low polarizability and a low refractive index. Inasmuch as the refractive index is a simple function of the dielectric constant of a substance, the same causes ought to produce the same effects: low values for both of these constants.

The values of AR_D cited by the American authors for the carbon fluorides, rising from 0.95 in the monofluorides to 1.23 in the other carbon fluorides, are in apparent contradiction with these arguments. In our opinion, this contradiction is the result of a misunderstanding. These values of AR_D were obtained by subtracting the products $2.418n_C + 1.100n_H$ from the values of MR_D for the substance, and dividing the remainder by the number of fluorine atoms in the molecule, in other words, the atomic refractions of the carbon and the hydrogen were assumed to be constants for all fluorohydrocarbons. That this is untrue for hydrogen is seen from the very fact that fluorohydrocarbons containing few hydrogen atoms in the molecule are soluble in alkalis, i.e., their hydrogen atoms are protonized. Since the polarizability of the proton is zero, the atomic refraction of protonized hydrogen atoms must be less than 1.100, and the difference must be shared among the fluorine atoms. The more hydrogen atoms in the molecule, the bigger is the difference accruing to a single fluorine atom, so that we may expect the true polarizability of fluorine in monofluorides (which is not directly measurable as yet) to exceed 1.23, as the polarizability of an atom linked to carbon by a heteropolar bond, rather than to equal 0.95.

Anomaly 6. The tearing away of molecules of the liquid through the surface film into the gas phase is prevented by the forces of mutual attraction (Van der Waals) and by interactions between the dipoles, the latter being most important. The introduction of a polar atom or group into a nonpolar molecule greatly lowers the vapor pressure of the substance, by no means proportionally to the increase in molecular weight. If we assume, as we have done above, that dipole interactions may be due to the partial dipole moments of the bonds as well as to the overall dipole moment of a particle, and that, moreover, the C-F bond in C_nF_{2n+2} is more homopolar than the C-H bond in C_nH_{2n+2} Anomaly 6 ceases to be an anomaly. The

volatility of carbon fluorides with balanced electron octets may be compared with the volatility of the heavy elements in the zero group of the Mendeleev system, which also have balanced octets in their outer electron shells.

Anomaly 7. must be viewed in the same light: if the C-F bonds in C_nF_{2n+2} are most homopolar, the variable that largely governs the volatility of a substance's molecules is the same for all isomers; whereas, if the C-H bonds in hydrocarbons are perceptibly heteropolar, the differences in their spatial coupling may yield varying values of the partial dipole moments of the parts of the molecule, thus resulting in different vapor pressures for various isomers of the hydrocarbons.

Anomaly 8. It follows from the foregoing that in fluorohydrocarbons whose molecules contain only a few hydrogen atoms the C-H bonds are highly polarized and the hydrogen atoms are protonized, resulting in a high overall dipole moment for the molecule and a corresponding decrease in its vapor pressure.

Anomaly 9. In the nitrile group the nitrogen atom is the negative end of the dipole, nitrogen being a negative substituent in the carbon chain. When this is so, it comes under the vicinal effect of at least four fluorine atoms, with the consequences resulting therefrom: the C-N bond becomes less heteropolar, and its partial dipole moment and the overall dipole moment of perfluoradiponitrile are diminished, resulting in an increase in its vapor pressure.

Anomaly 10. If we agree with the foregoing assertion: that the molecules of carbon fluorides are nonpolar both in the aggregate and partially, the high value of the temperature coefficient of expansion of the carbon fluorides follows at once, the molecules being held only by the Van der Waals forces, there being no dipole interaction.

Anomaly 11 is explainable analogously. The pattern of explanations of the anomalies exhibited by carbon fluorides put forth herein constitutes a qualitative essay to furnish a general picture of the problem from a given single standpoint (that of the vicinal effect). I submit this pattern for further discussion.

SUMMARY

A pattern of explanations of the anomalous physico-chemical properties of carbon fluorides is proposed, based upon the concept of the vicinal effect. According to this concept, the C-F bonds in carbon fluorides are entirely or almost entirely homopolar, with all the consequences resulting therefrom.

LITERATURE CITED

- [1] D.Tishchenko, J.Gen.Chem 9 1380 (1939).
- [2] D.Tishchenko and N.Zhokhovets, J.Gen.Chem 18, 23 (1948). (Submitted to the editors on Jan. 3, 1947).
- [3] Volkenshtein, Elyashevich, and Stepanov. Molecular vibrations. State Theoretical Engineering Press (1949).
- [4] The Chemistry of Fluorine, a symposium, Vol. I (Russ. ed.). Moscow (1948).
- [5] D.Tishchenko, J.Gen.Chem. 17, 897 (1947).
- [6] Heydweyller, Phys. Z., 26, 526 (1925).

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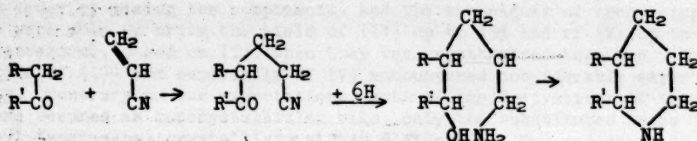
Received November 23, 1949.

SYNTHESES EMPLOYING ACRYLONITRILE

XIII. γ -ACETOBUTYRONITRILE AND ITS REDUCTION PRODUCTS

A.P. Terentyev and S.M. Gurvich

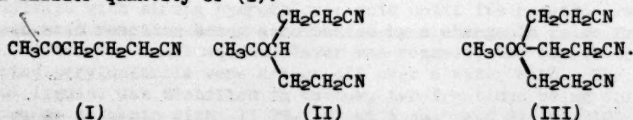
In several previous papers [1] A.P. Terentyev and his co-workers have investigated the cyanethylation reaction, various amines being reacted with acrylonitrile. A number of di- and polyamines have been synthesized by reducing the aminonitriles thus prepared. As we know, the cyanethylation reaction may be carried out with various other compounds that possess an active enough hydrogen atom. The cyanethylation reaction occurs readily when ketones, nitriles, some esters, etc. are used, addition products containing one or more molecules of acrylonitrile being secured [2]. We were interested in utilizing these compounds for further syntheses, first of all, in reducing them to the respective amines. If ketones, for instance, were used as the initial substances, this could provide a comparatively simple way of synthesizing ϵ -alkan-olamines, cyclization of which would yield homologs of piperidine:



We chose acetone as one of the simplest and most easily available ketones.

Brunson and his co-workers [3] effected the cyanethylation of acetone with acrylonitrile in the presence of trimethylbenzylammonium hydroxide. The sole individual product recovered and identified proved to be a tricyanethylation product of acetone, i.e., γ -aceto- γ -(2-cyanethyl)-pimelonitrile (III). As for products with a different degree of acetone cyanethylation, Brunson merely advanced the supposition that they were probably formed at the same time. Subsequently, Shannon [4] secured a patent for the synthesis of monocyanethylated acetone, i.e., γ -acetobutyronitrile (I), with 50% sodium hydroxide.

In the present research we have isolated and identified the monodi-, and tricyanethylation products of acetone, finding that the principal product is (III), followed by (II)- γ -acetopimelonitrile (a dicyanethylation product)- and a smaller quantity of (I):

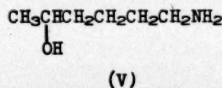
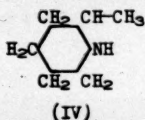


when sodium hydroxide is used as a catalyst, even with a large excess of acetone present.

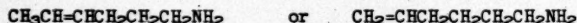
Raising the temperature and prolonging the reaction reinforces the above-mentioned tendency of several cyanethyl groups to enter the acetone molecule. We have proved that this assertion holds true for the 0-120° temperature range

with the acetone: acrylonitrile ratio ranging from 1.1 to 10.1 for mechanical stirring, and at any component proportions when no stirring is employed. The overall yield of cyanethylation products exceeded 50% in our experiments, including up to 8% of (I), up to 15% of (II), and over 24% of (III), based on the acrylonitrile, plus a certain amount of what was probably tetra- and pentacyan-ethylated acetone,¹ which was not analyzed further.

In reducing acetobutyronitrile we bore in mind the possibility of cyclization to homologs of piperidine, either during the reduction process proper as the result of the action of sodium alcoholate, as has been shown by Wohl and Maag [5], or by subsequently dehydrating the β -alkanolamine produced. The β -ketonitrile was reduced with metallic sodium in butyl alcohol: the reduction products were recovered, first as hydrochlorides, and then by fractionating the free bases prepared from these salts. The reduction products of (I) included α -pipercoline (IV) and 6-aminohexanol-2 (V):



which were isolated and identified. By varying the reduction conditions (temperature and order of mixing the components) and the techniques of recovering the bases, we were able to bring the yield of (IV) up to 15% and of (V) up to 17% of the theoretical, based on (I), when they were synthesized together. The identification of (IV) and especially of (V) encountered considerable experimental difficulty. Contrary to our expectations, most of the derivatives of these compounds were secured as noncrystallizing oils, only the substituted ureas (with α -naphthyl isocyanate) crystallizing without difficulty. Our endeavors to cyclize (V) to (IV) by distillation with solid potassium hydroxide met with failure; we did find, however, that a base with a characteristic amine odor and a boiling point below that of (V) was formed. We did not identify this compound, but it is not the same as (IV). Apparently, we secured one or a mixture of several unsaturated amines with the structure of:



as occurred in the research of Wohl and Maag [5].

EXPERIMENTAL

Reaction of acetone with acrylonitrile. 212 g (4 mols) of acrylonitrile was added in the course of an hour, with vigorous stirring, to 470 g (8 mols) of boiling acetone containing 4 g of solid sodium hydroxide. The mixture was heated for another 2 hours with a reflux condenser. After the mixture had cooled, it was acidified with strong hydrochloric acid until its reaction was acid, the change to an acid reaction being accompanied by a change in color from brick-red to orange. After the small aqueous layer was removed, the excess acetone and the unreacted acrylonitrile were driven off over a water bath. The residue, an oily yellow liquid, was distilled in vacuum, two fractions being collected, within a wide range to begin with: 1) 75-110° at 6 mm; and 2) 160-210° at 9 mm. The residue, which did not distill without decomposing and solidified upon cooling,

¹) These are the figures for tests run to increase the output of the mono- and dicyanethylated acetones; if we set as our objective the reacting of all the acrylonitrile, the overall yield of cyanethylation products would be close to 100%, though there would be practically no mono- or dicyanethylation derivatives among the reaction products.

constituted more than half of the quantity under distillation.

γ -Acetobutyronitrile (I). Fraction 1 was triply distilled in vacuum, the substance being collected in the 93-98° range at 6 mm; the yield was 35 g.¹

The product was finally refined by double distillation at atmospheric pressure. A colorless, oily liquid, with hardly any odor, slightly soluble in water, freely soluble in alcohol, ether, and acetone; it cannot be distilled with steam and exhibits the iodoform reaction. B.p. 238-240° at 764 mm.

d_4^{20} 0.9747; n_D^{20} 1.4330; MR_D 29.69; Calculated: 29.74

7.980 mg substance: 0.882 ml N_2 (25°, 740 mm); 5.740 mg substance: 0.646 ml N_2 (25°, 743 mm). Found %: N 12.33, 12.61. C_6H_9ON . Calculated %: N 12.62.

The semicarbazone consists of white leaflets, soluble in water. M.p. 131° (from alcohol).

1.816 mg substance: 0.547 ml N_2 (23°, 745 mm). Found %: N 34.05 $C_7H_{12}ON_4$. Calculated %: N 33.33.

γ -Acetopimelonitrile (II). Fraction 2 was triply distilled in vacuum, the substance being collected in the 196-199° range at 6 mm, the yield being 48.5 g. A yellowish odorless liquid with the viscosity of glycerol, sparingly soluble in water, freely soluble in alcohol and acetone. It exhibits the iodoform reaction.

d_4^{20} 1.0485; n_D^{20} 1.4780; MR_D 43.53; Calculated: 43.41.

6.960 mg substance: 1.047 ml N_2 (24°, 748 mm); 7.652 mg substance: 1.139 ml N_2 (24°, 748 mm). Found %: N 16.96, 16.84. $C_8H_{12}ON_2$. Calculated %: N 17.06.

γ -Aceto- γ -(2-cyanethyl)-pimelonitrile (III). The residue left after Fractions 1 and 2 had been distilled off constituted a dark, crystalline mass. Double recrystallization from water and methanol yielded snow-white crystals that were freely soluble in acetone, moderately soluble in hot water and in hot methanol, and sparingly soluble in cold water, ether, and benzene; m.p. 152°. The figure given in the literature is m.p. 154° [3].

3.185 mg substance: 0.559 ml N_2 (27°, 745 mm); 3.297 mg substance: 0.566 ml N_2 (22°, 745 mm). Found %: N 19.60, 19.48. $C_{12}H_{15}ON_3$. Calculated %: N 19.34

Reduction of γ -acetobutyronitrile (I). 21 g (0.9 gram-atom) of metallic sodium was added in the course of 15 minutes to a boiling solution of 17 g (0.15 mol) of the nitrile in 400 ml (4.5 mols) of absolute butyl alcohol. The mixture was then heated for another halfhour until all the sodium had dissolved; after it had cooled, it was diluted with water and acidified with strong hydrochloric acid until its reaction was pronouncedly acid, and then the layers were separated. The aqueous layer was evaporated to dryness, and the hydrochlorides extracted from the large mass of sodium chloride in an extractor with absolute ethyl alcohol. The acidulated layer of butyl alcohol was steam-distilled, the residue left in the distilling flask being evaporated to the consistency of a paste and then combined with the bulk of the hydrochlorides extracted from the aqueous layer. The free bases were recovered from the hydrochlorides by the use of an excess of sodium hydroxide under a layer of ether, a freezing mixture being applied. The free bases were extracted ten times with ether from the

¹) Shannon [4] gives only one constant for (I): b.p. 100-130° at 2 mm, which differs widely from our figure, the reliability of which is supported by the complete description of (I).

resultant paste of sodium chloride, the residue being distilled from a copper flask, and the distillate being saturated with solid sodium hydroxide and repeatedly extracted with ether. The ether extract was added to the main ether extract. The combined extracts were filtered and desiccated with fused potassium hydroxide. Most of the ether was driven off with a dephlegmator, the concentrated ether solution of the bases being finally desiccated with barium oxide and distilled in a current of nitrogen. Fraction 1: 118-120° at atmospheric pressure; weight 2.3 g.

α -Pipicoline (IV). Fraction 1 was triply distilled in a current of nitrogen. A mobile liquid with the odor of piperidine, avidly absorbing moisture and carbon dioxide from the air. P.p. 118-119° at 753 mm; d_4^{20} 0.8412; n_D^{20} 1.4430, which agrees with the figures in the literature [6, 7] M_p 31.25 $C_6H_{13}N$. Calculated: 31.31.

The picrate was prepared as yellow needles by adding the amine to a solution of picric acid in absolute benzene. M.p. 164° (from water). The figures given in the literature differ with each other and with our figure: m.p. 134-135° [6] and 127-128° [7].

4.000 mg substance: 0.602 ml N_2 (25°, 748 mm); 3.925 mg substance: 0.547 ml N_2 (26°, 751 mm). Found %: N 16.97, 16.90. $C_{12}H_{15}O_4N_4$. Calculated %: N 17.07

The hydrochloride was prepared by passing anhydrous hydrogen chloride through an ether solution of the amine. Transparent prisms, readily soluble in water and alcohol, slightly soluble in acetone. M.p. 207° (from dioxane), which agrees with the figures given in the literature [6, 7, 8].

4.496 mg substance; 0.405 ml N_2 (29°, 748 mm); 6.330 mg substance: 0.566 ml N_2 (26°, 748 mm). Found %: N 10.02, 9.95. C_6H_4NCl . Calculated %: N 10.33.

The oxalate was precipitated as a flocculent white precipitate when an ether solution of the amine was combined with an alcoholic solution of oxalic acid. It was recrystallized with ether from alcohol. Transparent clusters of needles (under the microscope). Softening point 108°, m.p. 125°.

The flavianate was precipitated as a noncrystallizing orange oil, soluble in alcohol and ether, by adding the amine to a solution of flavianic acid in absolute benzene.

Benzene sulfonyl chloride forms the corresponding derivative with the amine when 10% of an alkali or pyridine is present - a dark yellow oil that is insoluble in alkalies, but dissolves in alcohol and in ether.

α -Naphthyl isocyanate yields the corresponding substituted urea when absolute ether solutions of the two components are poured together: transparent crystals with a m.p. of 218° (from aqueous alcohol).

6-Aminoheptanol-2 (V). Fraction 2 was vacuum-distilled three times in a current of nitrogen. A colorless, mobile liquid with a faint amine odor that is freely soluble in water and alcohol, but sparingly so in ether. It avidly absorbs moisture and carbon dioxide. Its viscosity rises appreciably after it has been allowed to stand for 2 hours in the air. B.p. 98-100° at 6 mm; d_4^{20} 0.9365; n_D^{20} 1.4702; M_p 34.93. $C_6H_{15}ON$. Calculated: 34.98.

The hydrochloride was secured as transparent crystals by passing anhydrous hydrogen chloride through an ether emulsion of the alkanolamine. The crystals deliquesce as soon as they come into contact with the air; keeping the deliquesced

hydrochloride above sulfuric acid in a vacuum desiccator for a long time, as recommended by Krasussky [9] for the hydrochlorides of the α -alkanolamines, did not dehydrate the crystals.

The picrate and the flavinate settle out as oils, which we were unable to crystallize.

We managed to secure the oxalate in the crystalline state by pouring together an emulsion of the alkanolamine in ether and an alcoholic solution of oxalic acid. The flocculent white precipitate, which was readily soluble in water and alcohol, was recrystallized by precipitating it with ether from an alcoholic solution. Extremely minute needles (under the microscope). M.p. 100°. A mixture with hydrated oxalic acid (m.p. 101°) exhibited a sharp depression.

Reacting benzene sulfonyl chloride with the alkanolamine in an alkali or pyridine yields a yellow oil that is soluble in alcohol and in ether. It is also soluble in alkalis (enolization), being recovered unchanged upon acidulation.

α -Naphthyl isocyanate reacts exothermally with an alkanolamine when their ether solutions are poured together, forming crystals that are insoluble in water, ether, or carbon tetrachloride, moderately soluble in the lower alcohols, and freely soluble in acetone. M.p. 107° (from aqueous methanol).

4.380 mg substance: 0.392 ml N_2 (28°, 739 mm); 4.190 mg substance: 0.382 ml N_2 (28°, 739 mm). Found %: N 9.87, 10.06. $C_{25}H_{22}O_2N_2$. Calculated %: N 9.78.

SUMMARY

1. When acetone is cyanethylated, addition products of acetone containing one, two, or three molecules of acrylonitrile are formed simultaneously. The corresponding derivatives have been isolated and described.

2. Reducing γ -acetobutyronitrile with sodium in butyl alcohol yields 6-amino-hexanol-2 and its cyclization product: α -pipercoline.

LITERATURE CITED

- [1] A.P.Terentyev and Assoc., J.Gen.Chem. 12, 415 (1942); 16, 859 (1946); 17, 1632 (1947); 18, 82 (1948).
- [2] For a survey of the cyanethylation reaction cf A.N.Kost, Sci.Pap. Moscow State Univ, Vol. VI, No.131 (1950): Supplement to the work by Houben: Methods of organic chemistry (Russ. ed.), Vol.IV, Pt. 1, p. 1130; A.V.Belotsvetov, ibid., p.1034.
- [3] H.Bruson, T.Riener, J.Am.Chem.Soc. 64, 2850 (1942); H.Bruson, U.S.Patent 2311183; (1948); Ch. A., 37, 4500 (1943).
- [4] O.Shannon, U.S.Patent 2381371; (1945); Ch. A., 350 (1946).
- [5] A.Wohl, R.Maag, Ber., 43, 3280 (1910).
- [6] A.Lipp, Ann., 289, 210 (1896).
- [7] W.Marckwald, Ber., 29, 43 (1896).
- [8] A.Ladenburg, Sobeski, Ber., 42, 3153 (1909).
- [9] K.Krasussky and K.Kosenko, Ukrain. Chem. Jour. 4, 199 (1929).

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Received October 3, 1949.

ALKYL CARBONATES. II.

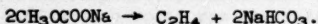
V.I. Kurov

Methylsodium carbonate CH_3COONa . The salt was prepared by a method similar to that used for producing ethylsodium carbonate [1]; passing carbon dioxide through sodium methylate. The salt's behavior with water and solvents is like that of ethylsodium carbonate, its specific gravity exceeding unity.

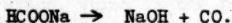
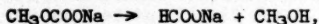
0.1292 g substance: 0.0930 g Na_2SO_4 ; 0.3332 g substance: 0.2412 g Na_2SO_4 . Found %: Na 23.31, 23.44. CH_3COONa . Calculated %: Na 23.46.

Thermal decomposition. 10 g of methylsodium carbonate, heated to $300-310^\circ$, yielded 2.58 g (recomputed value) of a combustible gas, 0.75 g of a liquid, and 6.10 g of a solid residue. Analysis of the gas (on a 100% basis) indicated: 84.5% CO_2 , 3.7% C_2H_4 , and 11.8% CO. The liquid, which had a sharp, acrid odor, was tested with ammoniacal silver nitrate; the test indicated the presence of formaldehyde, a silver mirror being formed. Besides the formaldehyde, water and methanol were found in the distillate. The gray residue was calcined in a platinum crucible, causing a loss of 7.28% in weight (organic content). The calcined residue was converted into sodium sulfate, 43.31% sodium being found upon analysis, which is equivalent to 43.40% of sodium in the sodium carbonate.

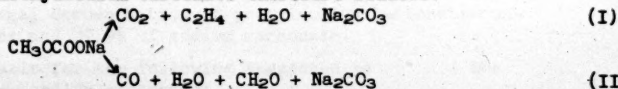
The analysis data indicate that the pattern of thermal decomposition of the methylsodium carbonate is as follows:



When NaHCO_3 is decomposed, it yields soda, carbon dioxide, and water, which hydrolyzes the methylsodium carbonate to form an alcohol:



Reacting with the carbon dioxide, the NaOH forms soda and water. (It is not impossible that the reaction also follows this course: $2\text{HCOONa} \rightarrow \text{H}_2 + \text{CO} + \text{Na}_2\text{CO}_3$.) The decomposition of methylsodium carbonate therefore follows:



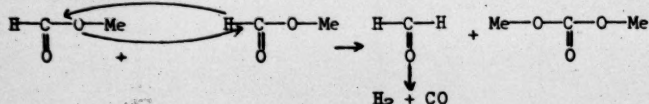
Decomposition takes place largely in accordance with Equation (I) when methylsodium carbonate is decomposed thermally. It is supposed that the carbon monoxide is not formed from the alcohol resulting from the hydrolysis of the methylsodium carbonate. During the thermal decomposition the methanol first turns into formaldehyde, which disintegrates quantitatively into carbon monoxide and hydrogen, but this requires either a high temperature, of the order of 500° , or the presence of a catalyst (copper and the like).

According to Hoffmann and Schumpelt [2], when sodium formate is decomposed thermally to yield carbon monoxide, the initial reaction is a displacement of the hydrogen atom within the sodium formate molecule, in accordance with the following reactions:

1. A shift of the hydrogen to the oxygen atom attached to the metal:
 $\text{HCOONa} \rightarrow \text{CO} + [\text{MeOH}]$, the MeOH yielding $\text{Me}_2\text{CO}_3 + \text{H}_2\text{O}$ in the presence of CO_2 .

2. Hydrogen atoms from two different sodium formate molecules join to form a hydrogen molecule and sodium oxalate: $2\text{HCOONa} \rightarrow \text{H}_2 + (\text{COONa})_2$.

3. The OMe group in the HCOOMe molecule is replaced by hydrogen from another molecule:



This reaction pattern is more applicable to divalent metals. Me_2CO_3 is further decomposed partially into CO_2 and Me_2O . The oxalates begin to break down at 160° .

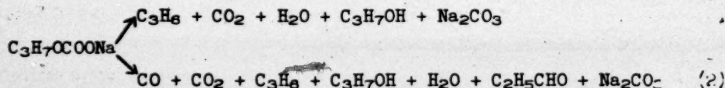
Gershkovich [3] supposes that the initial decomposition of oxalate yields carbon dioxide and the free metal (Na, K, Ca) which is readily oxidized, taking one oxygen atom from the carbon dioxide and thus forming carbon monoxide.

Propylsodium carbonate $\text{C}_3\text{H}_7\text{CCOONa}$. There is only one scanty reference to this salt [4]. Propylsodium carbonate has been prepared by passing carbon dioxide through sodium propylate.

0.1078 g substance: 0.0611 g Na_2SO_4 ; 0.3248 g substance: 0.1826 g Na_2SO_4 . Found %: Na 18.30, 18.18. $\text{C}_3\text{H}_7\text{CCOONa}$, Calculated %: Na 18.25.

The physical properties of propylsodium carbonate closely resemble those of the ethylsodium carbonate; it is fairly stable when heated up to 200° , no visible decomposition being observable. Appreciable decomposition takes place at 300° , the results at 350° being close to those secured at 300° . The thermal decomposition of 10 g of propylsodium carbonate yielded 1.87 g of gaseous substances, 3.40 g of liquids, and 4.60 g of a solid residue. Analysis of the gas (on a 100% basis) indicated: 34.3% carbon dioxide, 8.8% propylene, and 56.9% carbon monoxide. The liquid had a fragrant ethereal odor and exhibited the presence of an aldehyde when tested with fuchsin-sulfurous acid. When fractionated (boiling began at $89-90^\circ$), the bulk of the liquid distilled at $97-98^\circ$; d_4^{20} 0.824; d_4^{20} 0.8058, after dehydration, which is the figure for propyl alcohol. The chocolate-brown solid residue was spongy. Its analysis (by calcination) indicated that it contained 10.1% of organic matter. A weighed sample of the calcined residue was converted into sodium sulfate, the percentage of sodium carbonate indicating that it contained 43.3% sodium. Thus, the solid residue of the thermal decomposition of propylsodium carbonate contained 10.1% of organic matter and 89.9% of sodium carbonate.

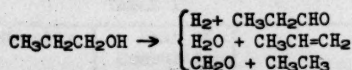
These figures are the basis for the following suggested partial thermal decomposition of propylsodium carbonate:



More of the salt is decomposed in accordance with Equation (2) than with Equation (1). It is supposed that the carbon monoxide is not formed from the alcohol resulting from hydrolysis of the propylsodium carbonate.

Nef [5] passed the vapor of propyl alcohol over pumice at $595-620^\circ$ and secured (in addition to 50% undecomposed alcohol) aldehyde, water, and benzene, the exhaust gases containing hydrogen, methane, carbon monoxide, and unsaturated hydrocarbons. At a still higher temperature acetylene and ethane are formed, as is indicated by Peutral [6]. These authors illustrate their

deductions from the analytical data by the following equations:



The formaldehyde may undergo further thermal decomposition to carbon monoxide and hydrogen, the ethane being decomposed to ethylene and acetylene. Mailheu and Renaudie [7] believe that the carbon monoxide is not split out from the alcohols directly, but rather after their preliminary dehydration to aldehydes or ketones; they also suppose that the alcohols are after dehydrated to hydrocarbons. In every case the carbon monoxide must be a by-product of the reaction, which is why it is recovered only in minute quantities. Kuznetsov [8] used platinum black as a catalyst in decomposing propylaldehyde at 250-390° and secured a gas that contained carbon monoxide.

Butylsodium carbonate $\text{C}_4\text{H}_9\text{OCOONa}$. We have been unable to find any data on this salt in the literature. We are the first to have synthesized the salt, by a method similar to that employed for preparing the propylsodium carbonate - passing carbon dioxide through sodium butylate. It is much harder to prepare both the sodium butylate and the butylsodium carbonate than is the case with the preceding homologs. Considerable difficulty being encountered in filtering and desiccating the product.

0.1332 g substance: 0.0682 g Na_2SO_4 ; 0.3892 g substance: 0.1973 g Na_2SO_4 . Found %: Na 16.56, 16.41. $\text{C}_4\text{H}_9\text{OCOONa}$, Calculated %: Na 16.43.

The physical properties of butylsodium carbonate resemble those of the propylsodium salt; it is freely soluble in water, the solution exhibiting an alkaline reaction owing to hydrolysis. It is almost insoluble in ethyl alcohol, benzene, chloroform, carbon disulfide, and acetone, though somewhat soluble in methanol. Its density is higher than unity. The physico-chemical data for butylsodium carbonate and other alkyl carbonates are given in greater detail below.

Butylsodium carbonate decomposes thermally much more slowly than other alkyl carbonates, practically no decomposition occurring at 300°. Decomposition was effected at 340-360°, 10 g of butylsodium carbonate yielding 0.81 g of gaseous products, 3.70 g of liquid, and 5.20 g of solids. Analysis (on a 100% basis) indicated: 52.1% CO_2 , 5.1% C_4H_8 , and 42.8% CO. The liquid is combustible, with a sharp aldehyde odor. It gave a positive test for an aldehyde with fuchsin-sulfurous acid. When distilled (boiling began at 112-114°), the bulk of the liquid distilled at 117-119° (d_4^{20} 0.814), which is the figure for butyl alcohol. The flask residue consisted of a few drops of a liquid with a pleasant ethereal fragrance and with a boiling point above 125°. The gray solid residue was calcined in a platinum crucible, the organic content being found to be 20.6% (including, apparently, tarring and polymer products of the aldehydes formed during the thermal decomposition of the butylsodium carbonate). Analysis of the calcined residue indicate that soda was present.

The following reaction pattern for the thermal decomposition of butylsodium carbonate (similar to the patterns put forward for methyl-, ethyl-, and propylsodium carbonates) is based upon the analytical data: $\text{C}_4\text{H}_9\text{OCOONa} \rightarrow \text{CO} + \text{CO}_2 + \text{C}_4\text{H}_8 + \text{H}_2\text{O} + \text{C}_4\text{H}_9\text{OH} + \text{C}_3\text{H}_7\text{CHO} + \text{Na}_2\text{CO}_3 (+\text{H}_2)$.

Most of the substances specified in these reactions have been determined quantitatively. Table 1 gives the heat capacities of the alkylsodium carbonates as calculated from the Kopp formula, their densities as determined with a pyknometer, and their heats of combustion.

TABLE 1

Formula	Heat Capacity	Density	Heat of Combustion, Cal/mol	Remarks
CH_3COONa	0.2974	1.955	146	The heats of evaporation of the water formed in the liquid state during the combustion of the alkylsodium carbonates have been deducted from the heats of combustion.
$\text{C}_2\text{H}_5\text{COONa}$	0.3173	1.799	290	
$\text{C}_3\text{H}_7\text{COONa}$	0.3329	1.786	432	
$\text{C}_4\text{H}_9\text{COONa}$	0.3543	1.630	577	

All of the above alkylsodium carbonates are insoluble (or only very slightly soluble) in benzene, chloroform, acetone, carbon disulfide, ethyl alcohol, or carbon tetrachloride, though they are somewhat more soluble in methanol.

Methyl-, ethyl-, propyl-, and butyl potassium carbonates. The synthesis of methyl- and ethylpotassium carbonates has been referred to in our first report. We have been the first to synthesize propylpotassium and butylpotassium carbonates. The thermodynamic data and the physico-chemical constants for all these salts, which are not to be found in the literature, are likewise given here for the first time. The alkylpotassium carbonates, like the alkylsodium carbonates, were prepared by passing carbon dioxide through the corresponding alcohols.

0.2192 g substance: 0.1669 g K_2SO_4 ; 0.2979 g substance: 0.2275 g K_2SO_4 . Found %: K 34.17, 34.27. CH_3COOK . Calculated %: K 34.25. 0.3124 g substance: 0.2138 g K_2SO_4 ; 0.2173 g substance: 0.1488 g K_2SO_4 . Found %: K 30.71, 30.73, $\text{C}_2\text{H}_5\text{COOK}$. Calculated %: K 30.50. 0.3096 g substance: 0.1910 g K_2SO_4 ; 0.2894 g substance: 0.1777 g K_2SO_4 . Found %: K 27.68, 27.56. $\text{C}_3\text{H}_7\text{COOK}$. Calculated %: K 27.50. 0.2543 g substance: 0.1452 g K_2SO_4 ; 0.2948 g substance: 0.1677 g K_2SO_4 . Found %: K 25.62, 25.53. $\text{C}_4\text{H}_9\text{COOK}$. Calculated %: K 25.03.

The physico-chemical data for these salts are given in Table 2.

TABLE 2

Formula	Heat Capacity	Density	Heat of Combustion, Cal/mol	Remarks
CH_3COOK	0.2554	2.555	128	The heats of evaporation of the water formed in the liquid state during the combustion of the alkylsodium carbonate have been deducted from the heats of combustion.
$\text{C}_2\text{H}_5\text{COOK}$	0.2774	2.373	271	
$\text{C}_3\text{H}_7\text{COOK}$	0.2950	1.979	414	
$\text{C}_4\text{H}_9\text{COOK}$	0.3095	1.960	558	

Methanol is the best solvent for alkylpotassium carbonates, the solubility of each salt exceeding 1% and that of the butylpotassium carbonate being of the order of 4%. The salts are insoluble in ethyl alcohol, acetone, benzene, carbon disulfide, or chloroform. Like the alkylsodium carbonates, the alkylpotassium carbonates are hydrolyzed when dissolved in water: $\text{ROCOOK} + \text{H}_2\text{O} \rightarrow \text{ROH} + \text{KHCO}_3$.

Butylrubidium carbonate $\text{C}_4\text{H}_9\text{COORb}$. There are no figures in the literature for this compound; we are the first to have synthesized it. Inasmuch

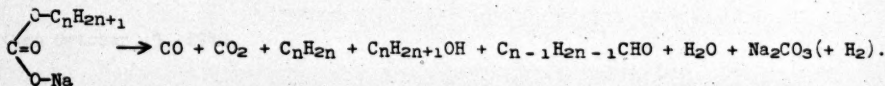
as metallic rubidium ignites readily when exposed to the air and reacts much more violently with alcohols than sodium and potassium do, considerable caution must be exercised in working with it (to avoid detonations or explosions). Metallic rubidium, deeply chilled to a low temperature, was added a little at a time to butyl alcohol, likewise strongly chilled. Carbon dioxide was then passed through the solution of rubidium butylate, the resulting butylrubidium carbonate being analyzed for its rubidium content; it was found to contain 42.45% rubidium. The calculated value was 42.19% Rb. As with the other alkylcarbonates, it is soluble in water, exhibiting a strongly alkaline reaction owing to hydrolysis: $C_4H_9OCCOORb + H_2O \rightarrow C_4H_9OH + RbHCO_3$.

The heat capacity of butylrubidium carbonate is 0.2393. Further details of the physicochemical constants of this salt will be given in forthcoming reports.

Figures 1 and 2 show the curves of the heat capacities, calculated by the Kopp formula, and the heats of combustion of the alkyl carbonates of the alkali metals of Group I in the Mendeleev periodic system of elements (lithium, sodium, potassium, rubidium). The heats of combustion of the lithium salts and of some of the rubidium salts have been calculated by extrapolation from the figures obtained for the sodium and potassium salts.

SUMMARY

1. Methyl-, propyl-, and butylsodium carbonates have been synthesized, the latter being produced for the first time. Their physicochemical and thermochemical properties have been investigated and their constants determined (density, heat of combustion, solubility, heat capacity, etc).
2. The analysis of the products of thermal decomposition has been utilized to establish the mechanism involved in the decomposition of the specified alkyl carbonates at 300° (at 340-360° for butylsodium carbonate), which is a dual one, carbon monoxide being evolved in one of the parallel reactions.
3. The general pattern of the reactions involved in the thermal decomposition of methyl-, ethyl-, propyl-, and butylsodium carbonates is set forth:



The evolution of carbon monoxide is attributable to secondary reactions (especially, decomposition of the sodium formate that may be an intermediate product in the decomposition of the alkylsodium carbonates).

4. Methyl-, ethyl-, propyl-, and butylpotassium carbonates have been synthesized, their physico-chemical and thermochemical properties have been investigated, and their constants established. Propylpotassium and butylpotassium carbonates have been synthesized for the first time.
5. Butylrubidium carbonate, $C_4H_9OCCOORb$, has been synthesized for the first time, its properties have been investigated, and some of its constants determined.

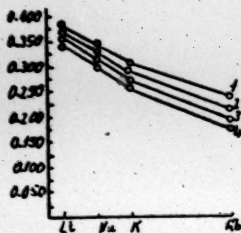


Fig. 1. Heat capacities of alkyl carbonates.

- 1) C_4H_9OCOO- , 2) C_3H_7OCOO- ,
3) C_2H_5OCOO- , 4) CH_3OCOO- .



Fig. 2. Heats of combustion (in kcal/mole).

- 1) C_4H_9OCOO- , 2) C_3H_7OCOO- ,
3) C_2H_5OCOO- , 4) CH_3OCOO- .

LITERATURE CITED

- [1] V. Kurov, Jour. Gen. Chem 21, 490 (1951)
- [2] Hoffman, Schumpelt, Ber., 49, 303 (1916).
- [3] Gershkovich, Z. allg. anorg. Ch. 115, 163 (1921).
- [4] C. Faurholt, J. Chr. Gjaldbaek, Dansk. Tids. Farm., 17, 213 (1943).
- [5] Mel, Ann., 318, 191 (1901).
- [6] Peutrel, Bull. Soc. chim., 35, 960 (1924); 27, 34 (1920).
- [7] Mailheu, Renaudie, Compt. rend., 185, 1598 (1927); 186, 238 (1928).
- [8] Kuznetsov, Jour. Russ. Phys. Chem. Soc. 45, 565 (1913).

Received October 15, 1949.

ALLYL REARRANGEMENTS

XIV. THE ACTION OF AMINES ON ISOMERIC METHOXYCHLOROPENTENES

A. N. Pudovik

Our preceding reports have described the reactions of various isomeric alkoxychloropentenes and dichlorobutenes with an alcoholic alkali, hydrosulfides of alkali metals, sodium derivatives of malonic and acetoacetic acids, salts of dialkylphosphorous acids, and other reagents [1].

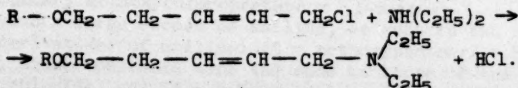
The present paper describes the results of a study of the reactions between various isomeric pairs of alkoxychloropentenes and primary or secondary amines.

Not much light is shed in the literature upon the reactions of amines with allylhalogen isomers. Meisenheimer and Link [2] were the first to study reactions of this sort, using cinnamyl chloride and pentenyl chloride; they concluded that the reactions with amines take place normally for primary chlorides and with a rearrangement for secondary chlorides. Jones, Lucey, and Smith [3] assert, however, that the reactions of allylhalogen isomers with amines depend largely upon the nature of the amines; the more basic the amine, the more anomalous will the reaction be. They found that the reaction of methylvinylethynylchloromethane with diethylamine is anomalous, involving a rearrangement, while its reaction with ammonia or aniline is normal, without any rearrangement.

We were greatly interested in a more systematic study of the reactions of the primary and secondary amines with the simplest allyl halogen compounds: $R-CH=CH-CH_2Cl$ and $R-CHCl-CH=CH_2$, where R is a saturated radical, and in determining the effect of the nature of the amines upon the course of these reactions. With this as our objective, we have made a study of the reactions of methoxy-, isopropoxy-, and butoxychloropentenes with diethylamine and of methoxychloropentenes with ethylaniline and aniline.

The procedure employed for these reactions was the usual one. The chloride was gradually added to an excess of the amine, after which the reaction mixture was heated over a water bath for several hours. Then it was treated with hydrochloric acid, the unreacted chloride being extracted with ether and the amine being recovered by adding a solution of sodiumhydroxide to the solution of its hydrochloride. After having been desiccated with alkali, the reaction products were vacuum-distilled from a small flask with a worm tower.

The reactions between diethylamine and the primary methoxy-, ethoxy-, and butoxychloropentenes yielded only a single product in each case, the structure of which corresponded to that of the original chloride.

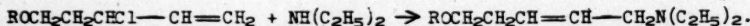


To establish the structure of the products, one of them - 1-methoxy-5-diethylaminopentene-3 - was oxidized with potassium permanganate; this yielded methoxypropionic acid, with a b.p. of 114° at 17 mm; n_D^{20} 1.4155, confirming the structure advanced for the product.

The constants of the products are listed in the following table:

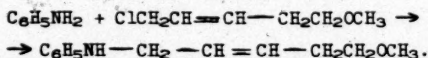
No.	Formula	Boiling point, °	n_D^{20}	d_4^{20}	MR _T		Per cent yield
					Found	Computed	
1	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{N}(\text{C}_2\text{H}_5)_2 \dots$	83(8 mm)	1.4410	0.8453	53.4	53.4	74
2	$(\text{CH}_3)_2\text{CHOCH}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{N}(\text{C}_2\text{H}_5)_2$	108-109(15 mm)	1.4380	0.8356	62.5	62.6	58
3	$n\text{-C}_4\text{H}_9\text{OCH}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{N}(\text{C}_2\text{H}_5)_2$	120-122(11mm)	1.4420	0.8367	67.3	67.2	82

We then made a study of the reaction of diethylamine with the secondary methoxy-, isopropoxy-, and butoxychloropentenes. These reactions yielded us products the constants of which were the same as those of the products secured from the respective primary chlorides. The product yields were 55-70% of the theoretical. No low-boiling fractions were found. These results indicate with a high degree of certainty that the reactions of the secondary methoxy-, isopropoxy-, and butoxychloropentenes with diethylamine are monomolecular, involving a complete allyl rearrangement:



Similar results were obtained when the isomeric methoxychloropentenes were reacted with ethyl aniline. The reaction of ethylaniline with the primary and secondary methoxychloropentenes yielded the same product in both cases: ethyl-(5-methoxypentenyl-2)-aniline, the constants of which were as follows: b.p. 159-161° (10 mm); n_D^{20} 1.5360; d_4^{20} 0.9886. The product yield was about 77% of the theoretical for both the primary and the secondary chloride. As in the case of diethylamine, the reactions were normal for the primary chloride and entirely anomalous for the secondary chloride, entailing an allyl rearrangement.

Interesting results were obtained in our study of the reactions of the isomeric methoxychloropentenes with aniline. Only a single product - (5-methoxypentenyl-2)-aniline - was secured when we reacted primary methoxychloropentene and aniline together, with a large excess of the latter in the reaction medium, the yield being 78.5%:



When there was insufficient aniline in the reaction medium (50% of the theoretical), the principal reaction product was a tertiary amine: di-(5-methoxypentenyl-2)-aniline, with a b.p. of 204° (10 mm); n_D^{20} 1.5330; d_4^{20} 1.0000, plus a negligible quantity of the secondary amine, 5-methoxypentenyl-2-aniline. In both cases the reaction was normal, without any rearrangement and with the formation of substitution products whose structure corresponded to that of the initial chloride.

When the secondary methoxychloropentene - 1-methoxy-3-chloropentene-4 - was reacted with a large excess of aniline, we secured two isomeric monosubstituted derivatives of aniline: (5-methoxypentenyl-2)-aniline, with a 50% yield, whose constants were the same as those of the product obtained from the primary chloride, and (3-methoxy-1-vinylpropyl)-aniline, with a 34.6% yield (b.p. 138°/10 mm; n_D^{20} 1.5390; d_4^{20} 1.0030).

When a large excess of the secondary chloride was used for the reaction, we got a low yield of di-(5-methoxypentenyl-2)-aniline, whose constants were likewise the same as those of the product secured from the primary chloride, in

addition to the two monosubstituted aniline derivatives specified above.

The reactions of 1 - methoxy - 3 - chloropentenyl - 4 with aniline apparently involve a combination of monomolecular and bimolecular mechanisms, thus resulting in the formation of products whose structures correspond to those of the two isomeric chlorides.

As we see it, the proposed mechanism for the reactions is the most likely for the cases in question, though it is not impossible that they involve an anomalous bimolecular substitution to some extent. Vinokurova and I [4] employed the latter mechanism to explain the reactions of magnesium with allyl halogen compounds, while Kepner, Winstein, and Young [5] have used it to explain the reactions of isomeric butenyl chlorides with sodium malonic ester; Catchpole, Hughes, and Ingold [6] consider it generally improbable, however, for reactions involving allyl halogen compounds. The absence of kinetic data on the reactions of amines with allyl halogen isomers makes it impossible to draw any more definite conclusions at the present time regarding the mechanisms involved in these reactions.

The structure of (3 - methoxy - 1 - vinylpropyl) - aniline has been established by oxidizing it with potassium permanganate. The oxidation products were proved to contain formic acid by reactions with silver oxide, mercuric chloride, and phenylhydrazine with nitroprusside.

The cited researches indicate that the reactions between amines and allyl halogen compounds of the $R - CHCl - CH = CH_2$ and $R - CH = CH - CH_2Cl$ types are largely governed by the nature of the amines. The reactions of the isomeric methoxy-, isopropoxy-, and butoxychloropentenes with secondary amines: diethylamine and ethylaniline, are normal for the primary allyl halogen isomers and quite abnormal, involving an allyl rearrangement, for the secondary ones. The reactions with the primary amine, aniline, are different: they are normal with primary methoxy-chloropentene and apparently of a combined ionic-molecular nature with the secondary methoxychloropentene, entailing a partial rearrangement and the formation of a large quantity of an anomalous product.

These results largely confirm and extend the conclusions reached by the authors of the papers cited regarding the effect of the nature of amines upon the course of their reactions with allyl halogen isomers, though they cannot be regarded as fully adequate for generalized conclusions. Further extensive study of the reactions of allyl halogen isomers, especially of those of the simplest type, with various primary amines is required.

EXPERIMENTAL

(With the participation of the student N. A. Kapitonova)

Action of diethylamine upon 1 - methoxy - 5 - chloropentene - 3. 20 g of 1 - methoxy - 5 - chloropentene - 3 was added gradually from a dropping funnel, with constant stirring, to 43.2 g of diethylamine placed in a round-bottomed flask. Crystals settled out, the entire mass crystallized toward the end of the addition of the chloride. The mass was heated for 10 hours over a water bath and then treated with 200 ml of dilute (1: 1) hydrochloric acid. The unreacted chloride was eliminated by extraction with ether, after which the solution was processed with alkali. The resulting amines were separated in a separatory funnel, the aqueous solution being extracted repeatedly with ether. The ether extracts were added to the separated amine layer, desiccated with fused alkali, and fractionated, yielding 2.25 g of a fraction with a b.p. of 81-83° (8 mm); n_D^{20} 1.4400 and 16.43 g of 1 - methoxy - 5 - diethylaminopentene - 3 (cf Table 1

for the latter's constants), after the ether and the unreacted diethylamine had been driven off.

0.7982 g substance: 8.76 ml H_2SO_4 ($T = 0.02535$). Found %: N 7.9. $\text{C}_{10}\text{H}_{21}\text{ON}$
Calculated %: N 8.2.

Action of diethylamine upon 1-methoxy-3-chloropentene-4. The reaction was carried out under the same conditions and with the same reagent quantities as with 1-methoxy-5-chloropentene-3 above, the sole difference being that the reaction mixture was heated for a longer time (20 hours), since the reaction with a secondary chloride is much slower. The crystals of the amine hydrochlorides did not settle out at once, but only after the reaction mixture had been heated over a water bath for 3-4 hours. After the reaction was complete, the reaction mass was processed as in the preceding experiment. Fractionation of the reaction products yielded 20.9 g of 1-methoxy-5-diethylaminopentene-3. B.p. $84-86^\circ$ (10 mm); n_D^{20} 1.4408; d_4^{20} 0.8467.

Oxidation of 1-methoxy-5-diethylaminopentene-3. Oxidation was carried out in a two-liter bottle, into which 600 ml of water and 12 g of 1-methoxy-5-diethylaminopentene-3 had been poured. 31.5 g of pulverized potassium permanganate was added a little at a time to the mixture, which was constantly and rapidly stirred. During the adding of the permanganate the bottle was cooled with running water. The reaction mixture was allowed to stand overnight at room temperature, the next day the aqueous layer above the manganese dioxide being found to be clear. The precipitate was filtered out and thoroughly washed with hot water. The aqueous salt solution was reduced to a volume of 40 ml and dilute (1:1) sulfuric acid was cautiously added to it until all the salts had been decomposed. The organic acids were extracted with several batches of ether, the ether layer was desiccated with calcium chloride, the ether was driven off above a water bath, and the residue was fractionated in vacuum. This yielded about 3 g of β -methoxypropionic acid, with a b.p. of 114° (17 mm) and n_D^{20} 1.4155. The residue in the flask turned into tar when heated further.

Action of diethylamine upon 1-isopropoxy-5-chloropentene-3. 20 g of the chloride was gradually added from a dropping funnel to 27 g of diethylamine. Then the reaction mixture was heated for 8 hours over a boiling water bath, after which it was processed as described for the preceding experiments. Fractionation of the reaction mixture yielded only one product: 14 g of 1-isopropoxy-5-diethylaminopentene-3 (Table 1, Formula 2).

0.9548 g substance: 9.12 ml H_2SO_4 ($T = 0.02535$). Found %: N 6.92.
 $\text{C}_{12}\text{H}_{25}\text{ON}$. Calculated %: N 7.03.

Action of diethylamine upon 1-isopropoxy-3-chloropentene-4. 20 g of 1-isopropoxy-3-chloropentene-4 was gradually added to 30 g of diethylamine. The crystals of the amine hydrochlorides did not begin to settle out at once, but only after the reaction mixture had been heated for several hours. Heating was continued for a total of 24 hours. The subsequent processing of the reaction mixture did not differ from that described for the preceding experiments. Fractionation of the reaction products yielded only one product: 15.1 g of 1-isopropoxy-5-diethylaminopentene-4. B.p. $101-102^\circ$ (10 mm); n_D^{20} 1.4380; d_4^{20} 0.8354. No low-boiling products were found.

Action of diethylamine upon 1-butoxy-5-chloropentene-3. This reaction was carried out with 20 g of 1-butoxy-5-chloropentene-3 and 36 g of diethylamine under conditions that resembled those described for the experiments using the isomeric methoxychloropentenenes. The reaction mixture was heated for 8 hours. Processing and fractionating the reaction products yielded 19.7 g of 1-butoxy-5-diethylaminopentene-3 (Table 1, Formula 3).

0.8556 g substance; 7.57 ml H_2SO_4 ($T=0.02535$). Found %: N 6.17. $\text{C}_{13}\text{H}_{27}\text{ON}$. Calculated %: N 6.57.

Action of diethylamine upon 1-butoxy-3-chloropentene-4. The reaction was carried out under conditions resembling those prevailing in the preceding experiment, and with the same quantities of reagents, the reaction mixture being heated for 24 hours. Only one product was secured as a result of the processing and fractionation of the reaction mixture: 14.1 g of 1-butoxy-5-diethyl-aminopentene-3. b.p. $120-122^\circ$ (11 mm); n_D^{20} 1.4420; d_4^{20} 0.8368.

Action of ethylaniline upon 1-methoxy-5-chloropentene-3. 71.6 g of ethylaniline and 20 g of 1-methoxy-5-chloropentene-3 were placed in a round-bottomed flask, and the reaction mixture was heated for 8 hours over a water bath. Then it was treated with dilute (1:1) hydrochloric acid, the unreacted chloride being eliminated by extraction with water, and the amine salts being decomposed by adding an alkali solution. Fractionation of the reaction products yielded only a single product: 25.3 g of ethyl-(5-methoxypentenyl-2) aniline, B.p. $159-161^\circ$ (10 mm); n_D^{20} 1.5360; d_4^{20} 0.9806.

1.1110 g substance; 9.26 ml H_2SO_4 ($T=0.02535$). Found %: N 6.07. $\text{C}_{14}\text{H}_{21}\text{ON}$. Calculated %: N 6.30.

Action of ethylaniline upon 1-methoxy-3-chloropentene-4. A mixture of 20 g of 1-methoxy-3-chloropentene-4 and 75 g of ethylaniline was heated for 30 hours over a water bath. The reaction mixture was processed as in the preceding experiment. Fractionation of the reaction products yielded only a single product: 22 g of ethyl-(5-methoxypentenyl-2)-aniline. B.p. $160-161^\circ$ (10 mm); n_D^{20} 1.5360; d_4^{20} 0.9797. No low-boiling fractions were recovered.

Action of aniline upon 1-methoxy-5-chloropentene-3. Test 1 - with an excess of aniline. 20 g of 1-methoxy-5-chloropentene-3 and 55.8 g of aniline were placed in a flask, and the reaction mixture was heated over a water bath for 9 hours. The reaction mixture crystallized almost completely toward the end of heating. It was cautiously transferred to a beaker containing 200 ml of dilute hydrochloric acid, the entire mass dissolving. The solution was extracted with ether and then treated with a concentrated solution of alkali. The resulting amines were desiccated with fused caustic potash and distilled in vacuum with a spiral still. After the unreacted aniline had been driven off, we secured 16.1 g of 5-methoxypentenyl-2-aniline. B.p. $163-164^\circ$ (10 mm); n_D^{20} 1.5458; d_4^{20} 1.0030.

1.0216 g substance; 9.85 ml H_2SO_4 ($T=0.02535$). Found %: N 6.99. $\text{C}_{12}\text{H}_{17}\text{ON}$. Calculated %: N 7.30.

Test 2 - with an excess of the chloride. 13.9 g of aniline and 40 g of 1-methoxy-5-chloropentene-3 were used for the reaction, the reaction mixture being heated over a water bath for 9 hours. Processing and fractionation of the reaction products yielded two products: 4.6 g of (methoxypentenyl-2)-aniline (b.p. $163-164^\circ$ at 10mm; n_D^{20} 1.5455; d_4^{20} 1.0025) and 13.2 g of di-(5-methoxypentenyl-2)-aniline (b.p. 204° at 10 mm; n_D^{20} 1.5330; d_4^{20} 1.0000).

1.0328 g substance; 6.79 ml H_2SO_4 ($T=0.02535$). Found %: N 4.76. $\text{C}_{18}\text{H}_{27}\text{ON}$. Calculated %: N 4.84.

Action of aniline upon 1-methoxy-3-chloropentene-4. Test 1 - with an excess of aniline. A mixture of 20 g of 1-methoxy-3-chloropentene-4 and 55.8 g of aniline was heated over a water bath for 9 hours, its subsequent processing following the usual lines. Fractionation of the mixture into a spiral still yielded two products:

- 1) 7.9 g of (3-methoxy-1-vinylpropyl)-aniline. B.p. $141-142^\circ$ (12 mm); n_D^{20} 1.5390;

° 1.0030.

0.9028 g substance; 8.48 ml H_2SO_4 ($T=0.02535$). Found % N 6.8 $C_{12}H_{17}ON$.
Calculated %: N 7.3.

2) 13.4 g of (5-methoxypentenyl-2)-aniline. B.p. 162-163° (10 mm); n_D^{20} 1.5455;
° 1.0035.

Test 2 - with an excess of the chloride. A mixture of 13.9 g of aniline and 40
of 1-methoxy-3-chloropentene-4 was heated for 20 hours over a water bath. Process-
ing and fractionating the reaction mixture yielded three products: 1) 3.5 g of
(5-methoxy-1-vinylpropyl)-aniline, with a b.p. of 138° (10 mm); n_D^{20} 1.5400;
2) 4.0 g of (5-methoxypentenyl-2)-aniline with a b.p. of 160-162° at 10 mm; n_D^{20} 1.5440
and 3) 5 g of di-(5-methoxypentenyl-2)-aniline with a b.p. of 204° at 10 mm;
° 1.5338.

Oxidation of (5-methoxy-1-vinylpropyl)-aniline. 18.21 g of finely pulverized
potassium permanganate was gradually added, with constant stirring and external
cooling of the flask with running water, to a mixture of 11 g of the product and
100 ml of water. After all the permanganate had been added, the mixture was set
aside to stand for 12 hours at room temperature. The manganese dioxide was filtered
out and washed with hot water, the aqueous solution being reduced to a volume of
10-40 ml and then treated with sulfuric acid. The acids were extracted with ether,
the ether extract was desiccated with calcium chloride, the ether was driven off,
and the residue was steam-distilled at atmospheric pressure. The distillate
exhibited a positive reaction for formic acid: adding silver oxide to it produced
a black deposit of silver and a partial silver mirror; adding a solution of mercuric
chloride threw down a white precipitate of calomel; adding magnesium, phenylhydraz-
ine and sodium nitroprusside to part of the distillate turned the solution blue.

SUMMARY

A study has been made of the action of isomeric methoxy-, isopropoxy-, and
utoxychloropentenenes upon diethylamine, ethylaniline, and aniline. It has been
shown that primary alkyl halogen isomers react normally with secondary amines,
no rearrangement taking place, the structure of the resultant products resembling
that of the respective original chloride.

The reactions between diethylamine and secondary allyl halogen compounds,
involve a complete allyl rearrangement, however, while the reaction with aniline
entails a partial rearrangement, apparently of a combined ionic-molecular nature.
The nature of the amine has a considerable effect upon the course of their reactions
with allyl halogen isomers.

LITERATURE CITED

- [1] A. N. Pudovik and B. A. Arbuзов, *Izv. USSR. Acad. Sci., Div. Chem. Sci.* 1946,
28, 544; 1948, 246; A. N. Pudovik, *Izv. USSR. Acad. Sci., Div. Chem. Sci.* 1948,
21, 530; 1949, 83; A. N. Pudovik and V. I. Nikitina, *J. Gen. Chem.* 19, 1034,
1179 (1949). 1)
[2] I. Meisenheimer and I. Link, *Ann.*, 479, 211 (1930).
[3] E. Jones, R. Lucey and P. Smith, *J. Chem. Soc.*, 1946, 540.
[4] A. N. Pudovik and G. M. Vinokurova, *J. Gen. Chem.* 19, 1882 (1949). 2)
[5] R. Kepner, S. Winstein and W. Young, *J. Am. Chem. Soc.*, 71, 115 (1949).
[6] A. Catchpole, E. Hughes and C. Ingold, *J. Chem. Soc.*, 1948, 4, 8.

Received Nov. 15, 1949.

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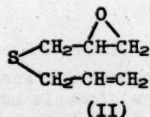
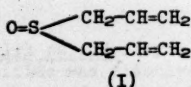
1) See Consultants Bureau English translation, p. 1025 and 1173.

2) See Consultants Bureau English translation, p. a-345.

THE STRUCTURE OF THE OXIDATION PRODUCTS OF DIALLYL SULFIDE

Yu. O. Gabel¹⁾ and L. F. Shpeier

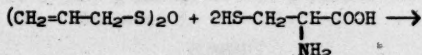
Levin was the first to describe the oxidation products of diallyl sulfide, $(\text{CH}_2=\text{CH}-\text{CH}_2)_2\text{S}$, in his investigation of the action of benzoyl hydrogen peroxide on some unsaturated sulfides [1]. He found that in this oxidation, one oxygen atom is first added to the sulfide molecule followed by a second oxygen atom, one sulfide molecule using up no more than two atoms of oxygen no matter what the concentration of the benzoyl hydrogen peroxide or the experimental conditions. Levin believes that the double bonds are unaffected in this instance, a sulfoxide being formed in the first stage of oxidation, and then a sulfone. He therefore attributes Structure (I) rather than (II), to the oxidation product of diallyl sulfide containing one atom of oxygen, on the basis of the following experimental observations:



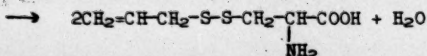
The substance he synthesized, with the empirical formula of $\text{C}_6\text{H}_{10}\text{SO}$, was a yellow oil with a b.p. of $107-109^\circ$ at 7-8 mm, freely soluble in water and in the usual solvents; he found its molecular refraction to be 38.2 [the calculated molecular refraction is 37.57 for Structure (I) and 36.67 for Structure (II)]. The substance does not throw down magnesium hydroxide from a solution of magnesium chloride nor ferric hydroxide from a solution of ferric chloride.

We have secured a product of the oxidation of diallyl sulfide with hydrogen peroxide that possesses the same empirical formula of $\text{C}_6\text{H}_{10}\text{SO}$, but different properties: it boils at 52° at 5-7 mm pressure, and is very slightly soluble in water, though freely soluble in alcohol, ether, and benzene. The data in the literature on the synthesis and the properties of sulfoxides, on the one hand, and of organic oxides of the ethylene oxide type, on the other, forced us to assume that the product we had synthesized was the sulfoxide, rather than Levin's substance.

Prilezhaev's researches have established that the oxidation of unsaturated compounds with benzoyl hydrogen peroxide results in the formation of organic oxides, i.e., the oxygen is added at the double bond [2], whereas oxidizing sulfides with hydrogen peroxide is a smooth and most customary method of securing sulfoxides. In contrast to organic oxides, sulfoxides are usually insoluble or very slightly soluble in water, as we found to be the case with our product, whereas Levin's product was freely soluble in water. One characteristic of sulfoxides is their ability to yield up an atom of oxygen readily being reduced thereby to sulfides. The reaction of allycine with cysteine has been described [3], in which the cysteine is oxidized by the allycine's oxygen, a crystalline product, S-thioallyl-cysteine, being formed:



¹⁾ Deceased.



We added a few drops of a solution of sodium nitroprusside and then our substance to a soda solution of cysteine. The intensive red color that appeared at first, due to the presence of the sulfhydryl group in the cysteine, vanished at once when the sulfoxide was added, a crystalline precipitate being thrown down. We decided to synthesize diallyl sulfide differently, eliminating any possibility of oxidizing the double bond, in order to establish finally the structure of the substance we had secured. In this respect our attention was drawn to the reaction between organomagnesium compounds and thionyl chloride, which results in the formation of the corresponding sulfoxide, according to the literature.

That is how Strécker synthesized diphenyl sulfoxide and dibenzyl sulfoxide [4]. We prepared allylmagnesium bromide from allyl bromide and magnesium [5] and then reacted it with thionyl chloride, resulting in the formation of a substance that was identical with the oxidation product of diallyl sulfide by hydrogen peroxide. This proves that in both cases we synthesized diallyl sulfoxide of Structure (I), the oxidation in Levin's research apparently having occurred at the double bond.

EXPERIMENTAL

1. Diallyl sulfide (by a modification of Hofmann's procedure [6]). 69.5 g of sodium sulfide was dissolved in 260 ml of boiling alcohol, and 35 ml of allyl bromide was then added gradually. The mixture was heated for 1 hour over a water bath with a reflux condenser and then poured into water. The resulting oil, which had the strong odor of garlic, was separated, dried with calcium chloride, and distilled in vacuum. The yield of diallyl sulfide was 8 g (34.6% of the theoretical); b.p. 35° at 5-7 mm.

2. Diallyl sulfoxide. a) From diallyl sulfide. 1 g of diallyl sulfide was dissolved in 2 ml of glacial acetic acid, and 1.2 ml of a 30% solution of hydrogen peroxide was added. The mixture warmed up considerably. After the mixture had cooled to room temperature, the reaction product was extracted with chloroform, the extract being washed with water, then dried with calcium chloride. Eliminating the chloroform yielded diallyl sulfoxide as an oil with a characteristic garlic odor. The yield was 0.45 g (39.5% of the theoretical); b.p. 52° at 5-7 mm.

0.1340 g substance; 0.2378 g BaSO₄; 0.1026 g substance; 0.1852 g BaSO₄; 0.1030 g substance; 0.1861 g BaSO₄. Found %: S 24.31, 24.73, 24.75. C₆H₁₀O₂S. Calculated %: S 24.61.

b) From allyl magnesium bromide. 4 g of metallic magnesium and a crystal of iodine were added to a solution of 15 ml of allyl bromide in 100 ml of absolute ether. The mixture was heated gently, setting off a violent reaction. After all the magnesium had dissolved, the mixture was chilled and 6 ml of thionyl chloride was added a drop at a time. Then the organomagnesium compound was decomposed with water acidulated with hydrochloric acid, and the sulfoxide was extracted with ether. The extract was dried with calcium chloride, and the ether was driven off, yielding an oil with a characteristic garlic odor. The yield of diallyl sulfoxide was 2.4 g (22.2% of the theoretical). B.p. 52-53° at 5-7 mm.

0.1728 substance; 0.3065 g BaSO₄; 0.1432 g substance; 0.2549 g BaSO₄. Found %: S 24.30, 24.39. C₆H₁₀O₂S. Calculated %: S 24.61.

SUMMARY

1. Oxidation of diallyl sulfide with hydrogen peroxide does not involve the

double bond, but results in the formation of diallyl sulfoxide.

2. Diallyl sulfoxide can be synthesized: a) by oxidizing diallyl sulfide with hydrogen peroxide, the yield being 39.5% of the theoretical and b) from allylmagnesium bromide and thionyl chloride, the yield being 22.2% of the theoretical.

LITERATURE CITED

- [1] Levin, J. *prek. Chem.*, (2) 127, 77-79 (1930).
- [2] Zimakov. Ethylene oxide, p. 104-106. State Chemical Press (1946).
- [3] Postovsky and Bednyagina, Prog. Chem. 16, 25 (1947).
- [4] Strecker, *Ber.*, 43, 1131-1133 (1910).
- [5] Grignard, *Ber.*, 36, 2898 (1903).
- [6] Hofmann, *Ann.*, 102, 291.

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Received October 2, 1949.

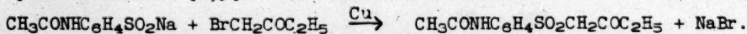
SYNTHESIS OF AMINOSULFIDES AND AMINOSULFONES

X. THE SYNTHESIS OF p-AMINOPHENYL β -KETOSULFIDE AND p-AMINOPHENYL

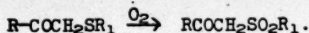
β -KETOSULFONES

I. Kh. Feldman and N. G. Prein

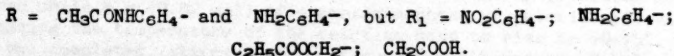
When halogen phenacyl derivatives are condensed with alkaline salts of sulfinic acids in water or alcohol containing copper powder, we get p-aminophenyl ketosulfones. This method was first proposed by Otto [1] and utilized repeatedly by other authors [2,3]. The reaction is as follows:



In the present research the β -ketosulfones were prepared by oxidizing β -ketosulfides, which were in turn prepared by condensing halogen derivatives of phenacyls with salts of the mercaptans:



As a result of the research we secured a series of β -ketosulfides and β -ketosulfones, in which



The sulfides and sulfones were oxidized by hydrogen peroxide in acetic acid. The reaction set in violently, the temperature of the reaction mixture being raised from 10-15° to 20-25°, sometimes even higher.

The reaction was conducted for 2-3 hours at a temperature no higher than 55°, as otherwise tarring sets in. The recovery and refining of the oxidized product were effective, the yields being as high as 80%. The resulting sulfides were yellow as a rule, turning white or a light cream when oxidized to sulfones.

The nitro group in the sulfides and sulfones was reduced by a method worked out in our laboratory, involving the use of hydrogen and Raney's nickel at room temperature at atmospheric pressure. Under these conditions the amount of catalyst employed equalled the weight of the substance to be reduced, reduction being smooth, with yields of 80-90%.

The acetyl groups in the respective acetaminoketosulfides and acetaminoketosulfones were saponified by 14% hydrochloric acid in water.

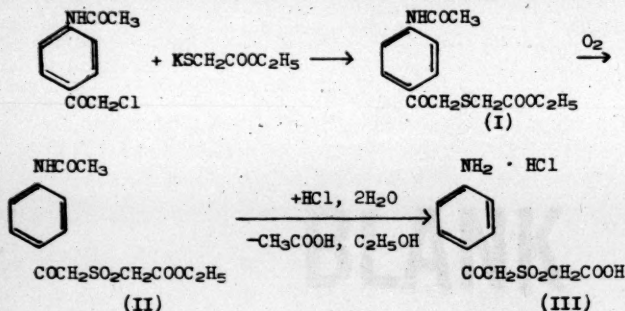
Troger and Hille [5] Michael [6], and other authors investigated the properties of the hydrogen atoms in the acid methylene group alongside the sulfinic group, proving that the methylenic hydrogen possessed high activity in the ketosulfones

and disulfones they had synthesized.

In order to demonstrate that the hydrogen atoms in the synthesized sulfone (VII) were active, we condensed it with dimethylaminobenzaldehyde in pyridine to which a few drops of piperidine had been added. The resulting substance contained a double bond. When its nitro group was reduced with hydrogen and Raney's Ni catalyst, the double bond was not hydrogenated, only the nitro group being reduced:

EXPERIMENTAL

Synthesis of *p*-aminophenacylsulfoglycollic hydrochloride:



p-Acetaminophenacyl ethyl glycollate sulfide. (I). 4 g (0.025 mol) of ethyl thioglycollate [7,8] was placed in a three-necked flask fitted with a stirrer, a thermometer and a dropping funnel, and 1.1 g (0.025 mol) of KOH in 30 ml of alcohol was added drop by drop in the cold. The resulting potassium mercaptide was stirred while 4 g (0.02 mol) of *p*-acetaminophenacyl chloride [9] was gradually added, causing the temperature of the reaction mass to rise to 40-45°. After this addition was completed, stirring was continued for 3 hours at 40-45°. Then the reaction mass was poured into 4 times its volume of water. The resulting cream-colored crystalline product was recrystallized from 70° alcohol; m.p. 90-92.5°. The synthesized substance weighed 5 g (89.2% of the theoretical). It was soluble in alcohol, acetone, and acetic acid, though insoluble in water, benzene, or petroleum ether.

Found %: N 4.74; S 10.33. $\text{C}_{14}\text{H}_{17}\text{O}_4\text{NS}$. Calculated %: N 4.88; S 10.45

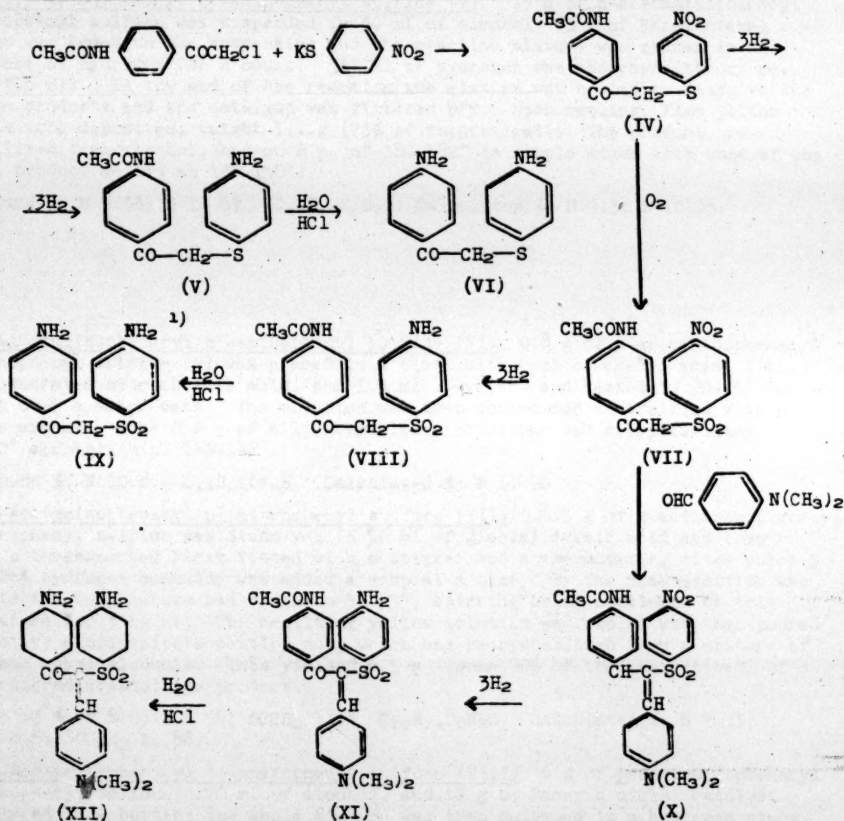
p-Acetaminophenacyl ethyl glycollate sulfone (II). 3 g (0.01 mol) of the sulfide synthesized above was dissolved in 20 ml of glacial acetic acid, placed in a flask fitted with a stirrer, a thermometer, and a dropping funnel. 2.5 ml of 26% hydrogen peroxide was added a drop at a time to the solution without the application of any heat. When all the perhydrol had been added, the temperature had risen to 50-55°, and the mixture was stirred at this temperature for 2 hours. When the reaction was over, the mass was chilled and then poured into three times its volume of water, a cream-colored precipitate being thrown down. The yield was 1.9 g (59%). The m.p. was 169-170° after crystallization of the precipitate from 70° alcohol. It was soluble in alcohol, acetone, and acetic acid.

Found %: N 4.16; C 52.03; H 5.47; S 9.71. $\text{C}_{14}\text{H}_{17}\text{O}_6\text{NS}$. Calculated %: N 4.25; C 51.7; H 5.5; S 9.78

p-Aminophenacetylsulfoglycollic Hydrochloride (III). 2 g of the sulfone synthesized above was heated with 20 ml of 14% hydrochloric acid over a water bath for 90 minutes. When the reaction was over and the solution cooled down, grayish crystals of the hydrochloride (0.4 g) settled out; they were soluble in water, alkalies, alcohol, and acetone, and insoluble in ether, benzene, or chloroform. Evaporating the filtrate yielded another 0.8 g of the hydrochloride, somewhat more highly contaminated. The total yield was 1.2 g (70.8% of the theoretical). The melting point was 190-191° after recrystallization from alcohol.

Found %: N 4.46; Cl 11.70. $C_{10}H_{12}O_5NSCl$. Calculated %: N 4.31; Cl 11.86

Synthesis of p-Aminophenacyl p'-Aminophenyl Sulfide (VI) and Sulfone (IX),



¹ Product (IX) had been previously synthesized by another method [1].

p-Acetaminophenacyl p'-nitrophenyl sulfide (IV). 1.1 g (0.02 mol) of KOH was dissolved in 3 ml of alcohol contained in a three-necked flask fitted with a stirrer and a thermometer, and 3.1 g (0.02 mol) of p-nitrophenylthiol [10] was added. The red solution of the potassium salt of p-nitrophenylthiol resulted, and 4.2 g (0.02 mol) of acetaminophenacyl chloride was then gradually added to it. When all the chloride had been added, the red solution of the potassium mercaptide turned yellow, and then a copious precipitate began to settle out. Stirring and heating were continued at 55° for 3 hours. This yielded 4.9 g of the dark-yellow p-acetaminophenacyl p'-nitrophenyl sulfide, the yield being 74% of the theoretical. It was recrystallized from 70° ethyl alcohol; yellow needles with a m.p. of 186-187°.

Found %: N 8.34; S 9.84. $C_{15}H_{14}O_4N_2S$. Calculated %: N 8.48; S 9.70.

p-Acetaminophenacyl p'-aminophenyl sulfide (V). 15 g of p-acetaminophenacyl p'-nitrophenyl sulfide was suspended in 30 ml of alcohol. 3 g of Raney nickel catalyst was added to the suspension and the reaction mixture was shaken in an atmosphere of hydrogen for 2 hours. 317 ml of hydrogen was absorbed (theory requires 305 ml). At the end of the reaction the mixture was heated to dissolve the reaction products and the catalyst was filtered off. Upon cooling, fine yellow crystals were deposited; weight 1.1 g (73% of theoretical). The product, recrystallized from alcohol, had an m.p. of 180-182° (a sample mixed with some of the initial product melted at 124-150°).

Found %: N 9.33; S 10.67. $C_{16}H_{16}O_2N_2S$. Calculated %: N 9.3; S 10.25.

p-Acetaminophenacyl p'-aminophenyl sulfide (VI). 0.8 g of p-acetaminophenacyl p'-aminophenyl sulfide (V) was placed in a flask with 6 ml of acetic acid, 1 ml of concentrated hydrochloric acid, and 1.5 ml of water, and heated to 70-75° for 2 hours over a water bath. The solution was then cooled and neutralized with aqueous ammonia. The 0.2 g of a light-yellow precipitate was recrystallized from 70° alcohol; m.p. 140-142°.

Found %: N 10.8. $C_{14}H_{14}ON_2S$. Calculated %: N 10.96.

p-Acetaminophenacyl p'-nitrophenyl sulfone (VII). 6.5 g of p-acetaminophenacyl p'-nitrophenyl sulfide was dissolved in 50 ml of glacial acetic acid and then put in a three-necked flask fitted with a stirrer and a thermometer, after which 5 ml of 26% hydrogen peroxide was added a drop at a time. By the time addition was complete the temperature had risen to 50-55°, stirring being continued at this temperature for 3 hours. The resulting yellow solution was cooled and then poured into water; a precipitate settled out, which was recrystallized from a mixture of butyl and ethyl alcohols. This yielded 6.5 g (some 90% of the theoretical) of a cream-colored crystalline product.

Found %: N 8.0; S 8.94; $OCCH_3$ 11.4. $C_{16}H_{14}O_5N_2S$. Calculated %: N 7.73; S 8.84; $OCCH_3$ 11.88.

p-Acetaminophenacyl p'-aminophenyl sulfone (VIII). 6 g of p-acetaminophenacyl p'-nitrophenyl sulfone, 170 ml of alcohol, and 12 g of Raney's nickel catalyst were placed in a bottle; the whole mixture was then agitated in a hydrogen atmosphere for 3 hours, the theoretically required quantity of 1050 ml of hydrogen being absorbed. Inasmuch as the precipitate contained the hydrogenation product together with the catalyst, the reaction mixture was heated until the precipitate

dissolved, the catalyst being filtered out of the solution and part of the alcohol being driven off. A total of 3.9 g of the product crystallized out (70% of the theoretical); its m.p. was 147-149° after recrystallization from alcohol. It was soluble in alcohol, ethyl acetate, acetone, and acetic acid.

Found %: N 8.36; S 9.57. $C_{18}H_{18}O_4N_2S$. Calculated %: N 8.43; S 9.63.

The p-acetaminophenacyl p'-aminophenyl sulfone was saponified by a mixture of hydrochloric and acetic acids. This yielded p-aminophenacyl p'-aminophenyl sulfone (IX) - a product with a m.p. of 216-217°, which was the same as the one described previously [1].

The 2-p-Acetaminobenzoyl 2-p'-nitrophenyl sulfone of 1-p'-dimethylamino-phenyl ethylene (X). 1.8 g of p-acetaminophenacyl p'-nitrophenyl sulfone (VIII), 0.75 g of dimethylaminobenzaldehyde, 7 ml of pyridine, and 2 drops of piperidine were placed in a round-bottomed flask. The whole mixture was then heated for 10 hours with a reflux condenser over an oil bath. Then the reaction mass was treated with 1% hydrochloric acid. This yielded a brick-colored product, which was crystallized from aqueous alcohol, its m.p. then being 76-78° (a fusion sample mixed with dimethylaminobenzaldehyde had a m.p. of 48-52°). The yield was 0.6 g.

Found %: N 8.42; S 6.42. $C_{25}H_{23}O_6N_3S$. Calculated %: N 8.51; S 6.49.

2-p-Acetaminobenzoyl 2-p'-aminophenyl sulfone of 1-p'-dimethylaminophenylethylene (XI). 1.2 g of the 2-p-acetaminobenzoyl 2-p'-nitrophenyl sulfone of 1-p'-dimethylaminophenylethylene (X), 40 ml of alcohol, and 2.4 g of Raney's nickel catalyst were placed in a bottle; the reaction mixture was agitated in an atmosphere of hydrogen for 3 hours, the theoretically required 168 ml of hydrogen being absorbed. The mixture was then heated until the reaction product dissolved completely. The catalyst was filtered out, 0.65 g of a finely crystalline, yellow-green product crystallizing out of the solution. The yield was 58%. When recrystallized from alcohol, it had a m.p. of 139-141°; it was soluble in dilute hydrochloric acid, acetone, and ethyl acetate; much less so in alcohol.

Found %: S 7.13. $C_{25}H_{25}O_4N_3S$. Calculated %: S 6.91.

2-p-Aminobenzoyl 2-p'-aminophenyl sulfone of 1-p'-dimethylaminophenylethylene (XII). 4 g of the 2-p-acetaminobenzoyl 2-p'-aminophenyl sulfone of 1-p'-dimethylaminophenylethylene (XI) was placed in a round-bottomed flask together with 10 ml of acetic acid and 10 ml of concentrated hydrochloric acid; the mixture was heated to 70-75° over a water bath. Everything dissolved within 6 hours. The solution was cooled and then neutralized with a 5% solution of sodium hydroxide, yielding 1.2 g of product; the m.p. was 160-162.5° after recrystallization of 70° alcohol. It was soluble in dilute hydrochloric acid, acetic acid, pyridine, acetone, and alcohol; insoluble in water or benzene.

Found %: S 7.39. $C_{23}H_{23}O_3N_3S$. Calculated %: S 7.5.

SUMMARY.

1. Several aromatic and aliphatic-aromatic β -ketosulfides have been synthesized, their oxidation yielding the corresponding aromatic and aliphatic-aromatic β -ketosulfones, not hitherto described in the literature.
2. The feasibility of reducing sulfides with Raney's nickel catalyst, pointed out by one of the present authors previously [11], has been confirmed.
3. The condensation product of p-dimethylaminobenzaldehyde with the β -ketosulfone at the acidic methylene group has been synthesized; this bears out the previously published papers on the activity of the hydrogen atoms in this group.

LITERATURE CITED

- [1] R.Otto and W.Otto, J. prak. Chem. (2), 36, 401 (1887).
- [2] J.Troger and T.Bolm, J.pr.Chem., (2) 55, 398 (1897). J.Troger and Unger, J. pr Chem, (2) 112, 243 (1926); J.Troger and O.Beck, J. pr. Chem, 87, 289 (1913).
- [3] A.Goldberg and Besly, J. Chem. Soc., 1945, 566.
- [4] D.A.Delise, Ann., 260, 10 (1890).
- [5] J.Troger, Hille, J.prak.Chem., 71, 201 (1905).
- [6] Michael, Comly, Ber., 10, 2300 (1883).
- [7] Klasson, Tor, Carlson, Ber., 39, 732 (1906).
- [8] L.Carius, Ann., 124, 43 (1862).
- [9] Kunczell, Ber., 33, 2644 (1900).
- [10] Th. Zincke, S.Lenhardt, Ann., 400, 6 (1913).
- [11] I.Feldman, Proc. USSR Acad. Sci. 65, 857 (1949).

The S. Ordzhonikidze All-Union Research
Institute of Pharmaceutical Chemistry.

Received June 27, 1949.

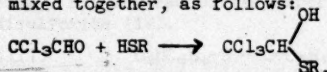
SYNTHESIS OF AMINOSULFIDES AND AMINOSULFONES

XI. THE SYNTHESIS OF 1,1,1-TRICHLORO-2-HYDROXYETHANE-(p-NITROPHENYL) SULFIDE, ITS ACETOXY DERIVATIVE, AND ITS SULFOXIDE

I.Kh. Feldman and T.I. Gurevich

Continuing our research [1] on a method of synthesizing β -aminosulfides and β -aminosulfones, we made a study of the condensation products of chloral and p-nitrophenylthiol.

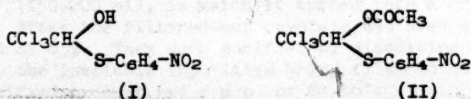
We know that chloral reacts with thiols when equimolecular quantities of the two substances are merely mixed together, as follows:



E. Baumann [2] secured compounds of this sort by reacting chloral with phenylthiol or bromophenylthiol; they are unstable, cannot endure heating, and break down when acted upon by alkali solutions.

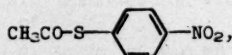
We condensed chloral with p-nitrophenylthiol, passing anhydrous hydrogen chloride through a mixture of these products at 55-60°, no solvent being employed, as well as in acetic anhydride. This reaction does not take place in benzene or dichloroethane. When we carried out the reaction without any solvent, we secured 1,1,1-trichloro-2-hydroxyethane-(p-nitrophenyl) sulfide (I).

When the reaction was carried out in acetic anhydride, the condensation (I) was accompanied by the acetylation of the resultant product, yielding 1,1,1-trichloro-2-acetoxyethane-(p-nitrophenyl) sulfide (II):



Both of these compounds are highly unstable, this being particularly true of (I): alkalis break them down into mercaptides; when these products are crystallized from alcohol, they decompose in part, forming a p,p'-dinitrodiphenyl disulfide. The synthesized products (I) and (II) were purified by dissolving them in ether at room temperature, filtering out the insoluble impurities, and evaporating the ether. Even this procedure did not purify Compound (I) completely, though Compound (II) was recovered in a purer state.

When the hydroxyl group in Compound (I) was acetylated to produce Compound (II) the molecule was ruptured, yielding a p-nitrophenylacetic thioether:



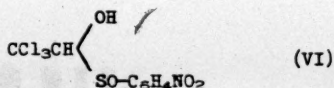
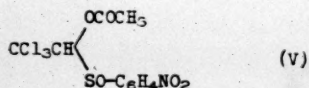
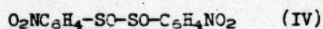
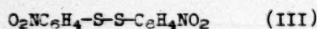
which was identified by analyzing its sulfur and nitrogen content and by the melting point of a fusion sample mixed with the known preparation.

Oxidizing Compound (I) with perhydrol at room temperature in acetone cleaved the molecule, yielding the p,p'-dinitrodiphenyl disulfide (III), which was isolated and identified by the melting point of a fusion sample mixed with the known product. Oxidation with perhydrol in glacial acetic acid and acetic anhydride likewise

resulted in cleavage of the molecule, yielding the p,p'-dinitrodiphenyl disulfide (IV). The latter was identified by analyzing it for its sulfur and nitrogen content and by the melting point of a fusion sample mixed with known dinitrodiphenyl disulfide.

Product (II) cannot be oxidized with perhydrol in acetone at room temperature, the initial 1,1,1-trichloro-2-acetoxyethane-(p-nitrophenyl) sulfide being recovered unchanged. When we oxidized Compound (II) with perhydrol in a mixture of glacial acetic acid and acetic anhydride, and when we oxidized it with chromic anhydride in glacial acetic acid, we secured 1,1,1-trichloro-2-acetoxyethane-(p-nitrophenyl) sulfoxide (V).

An attempt to oxidize Compound (V) further to the corresponding sulfone met with failure. Inasmuch as we were unable to oxidize Compound (I) to the sulfoxide (VI) or to secure the latter compound by saponifying the acetyl group in Compound (V), we effected the saponification by a mixture of concentrated hydrochloric and 80% acetic acids. But instead of the expected sulfoxide, we secured p,p'-dinitrodiphenyl disulfide (IV).



EXPERIMENTAL

1,1,1-Trichloro-2-hydroxyethane-(p-nitrophenyl) sulfide (I). 14.7 g of chloral (0.1 mol) and 15.5 g of p-nitrophenylthiol (0.1 mol) were placed in a three-necked flask fitted with a reflux condenser, a thermometer, and an inlet tube for anhydrous hydrogen chloride. Anhydrous hydrogen chloride was passed through the mixture for 2 hours, the temperature of the mixture being maintained at 55-60° by heating over a water bath. When the reaction was over, the mixture was poured into cold water (150-200 ml), in which it turned into a crystalline mass within a short time. After the filtered-out crystals had been desiccated, they weighed 19 g, a yield of 63%. They were purified by dissolving them in ether at room temperature, the insoluble impurities being filtered out, and the ether evaporated. The purified product had a m p of 64-66°.

Found %: S 10.11; N 4.92; Cl 35.35. $\text{C}_8\text{H}_8\text{O}_3\text{NSCl}_3$. Calculated %: S 10.57; N 4.62; Cl 35.20.

1,1,1-Trichloro-2-acetoxyethane-(p-nitrophenyl) sulfide (II). 14.7 g (0.1 mol) of chloral, 15.5 g (0.1 mol) of p-nitrophenylthiol, and 30 ml of acetic anhydride were placed in a three-necked flask fitted with a reflux condenser, a thermometer, and a gas-inlet tube. Anhydrous hydrogen chloride was passed through this mixture at 55-60° for 2 hours, after which the mixture was poured into 200 ml of cold water. The mass crystallized after some time had elapsed, the crystals being filtered out, washed with water, and desiccated. This yielded 26 g, or 75% of the theoretical. Purification with ether as described above yielded a product with a m.p. of 68-69°.

Found %: S 9.35; N 4.25; Cl 30.70. $\text{C}_{10}\text{H}_8\text{O}_4\text{NSCl}_3$. Calculated %: S 9.28; N 4.07; Cl 30.91.

1,1,1-Trichloro-2-acetoxyethane-(p-nitrophenyl) sulfoxide (V). 3.5 g (0.01 mol) of 1,1,1-trichloro-2-acetoxyethane-(p-nitrophenyl) sulfide, 25 ml of glacial acetic acid, and 5 ml of acetic anhydride were placed in a three-necked flask fitted with a stirrer, a thermometer, and a dropping funnel. The mixture was

stirred and chilled to 5-8°, and 7 ml of 29% perhydrol was added drop by drop at that temperature. After all the perhydrol had been added, the mixture was gradually heated to 50° and then stirred for 3 hours at this temperature. Everything dissolved in about one hour after the start of heating, after which a white crystalline precipitate began to settle out. When the reaction was over, the precipitate was filtered out and washed twice on the filter with 6-8 ml of ether each time. The yield of the sulfoxide was 2.1 g or 58%. The m.p. of 119-120° did not change after crystallization from glacial acetic acid. Found %: S 8.70; N 3.84. Cl 29.00. $C_{10}H_9O_2NSCl_3$. Calculated %: S 8.87; N 3.88; Cl 29.54.

SUMMARY

1. Condensing chloral with p-nitrophenylthiol yielded the addition product of 1 mol of chloral plus 1 mol of the thiol (no water being evolved). When the condensation was effected in acetic anhydride, the condensation was accompanied by acetylation of the hydroxyl group.
2. The unacetylated addition product of the thiol and chloral is unstable, breaking down when attempts are made to acetylate or oxidize it, even at room temperature.
3. The acetylated condensation product is somewhat more stable, its oxidation yielding the respective sulfoxide. Like the unacetylated product, however, it breaks down when heated or when exposed to the action of alkali solutions.

LITERATURE CITED

- [1] I.Kh.Feldman and T.I.Gurevich, J.Gen.Chem., 21, 1540 (1951).¹⁾
- [2] E.Baumann, Ber., 60, 883 (1885).

The S.Ordzhonikidze All-Union Research
Institute of Pharmaceutical Chemistry.

Received October 23, 1949.

¹⁾ See Consultants Bureau English translation, p. 1689.

THE ADDITION OF ANILINE AT THE DOUBLE BOND OF OLEFINS IN THE PRESENCE OF HETEROGENEOUS CATALYSTS

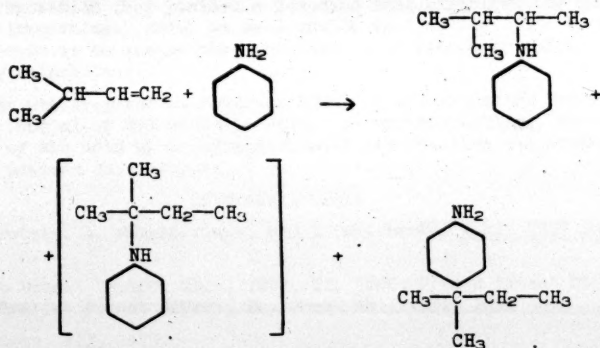
N.N.Vorozhtsov, student,¹⁾ and I.I.Ioffe

There are not many papers in the literature dealing with the reactions of aniline with olefins above heterogeneous catalysts. Only recently did K.Lavrovsky and his co-workers publish a report on the catalytic alkylation of aniline by *n*-butene [1]. This problem is also touched upon in several patents [2].

We have made a study of the reaction of aniline with isopropylethylene in the gas phase above a kaolin catalyst activated by sulfuric acid. The reaction was carried out in an autoclave at a temperature of 260°, the pressure being 30 atmospheres, the catalyst being in the vapor space.

As our investigations have shown, aniline, in contrast to ammonia, is added to olefins at the double bond, yielding the corresponding alkylamine. This is largely paralleled by the alkylation of the carbon atom in the ring adjacent to the amino group. When no catalyst was employed, all we got was a negligible quantity of *p*-isoamylaniline. It is quite possible that aniline can be added to olefins without any catalyst, but the per cent conversion is so low that we have been unable to detect the resultant *N*-alkylanilines.

In our experiments, the reaction of isopropylethylene with aniline in the presence of activated kaolin yielded tertiary *p*-amylaniline and a mixture of secondary *N*-alkylanilines. The latter included, we found, 2-methyl-3-phenylaminobutane and apparently 2-methyl-2-phenylaminobutane.



In addition, the reaction mass yielded various quantities of diphenylamine after every test, which was highly contaminated with substances of unknown composition.

The formation of tertiary *p*-amylaniline and 2-methyl-2-phenylaminobutane when isopropylethylene is reacted with aniline is due either to the isomerization of the alkyl anilines produced by the addition of aniline to isopropylethylene or by the prior isomerization of the isopropylethylene to trimethylethylene, the latter explanation being more likely.

¹⁾ Deceased.

As for the yields of the N-alkylanilines, they were low in our experiments, amounting to no more than 2%, based on the contaminated aniline. At the same time as much as 14.5% of p-amyraniline was formed.

EXPERIMENTAL

20 g (0.3 mol) of isopropylethylene and 55 g (0.59 mol) of aniline were heated together for 13.5 hours in an autoclave to a temperature of 250-260° and at a pressure of 29-25 atm, activated kaolin being employed as the catalyst. The catalyst was placed in the autoclave in such a way as to be in the gas phase of the reaction mixture.

After the reaction mass had cooled down, it was taken from the autoclave and acidified dilute hydrochloric acid until its reaction with Congo red was clearly acid, and the catalyst was filtered out. After filtration the catalyst was transferred to a distilling flask containing alkali, and the amines absorbed to it were driven off with steam.

The slight amount of polymer hydrocarbons was eliminated from the acid filtrate, which was then alkalized, the amines that separated out being combined with the amines in the distillate. The amine mixture was then desiccated with calcined potash, and the bulk of the aniline was driven off by distillation. The p-amyraniline was recovered as an insoluble sulfate (8.8 g) and identified as its acetyl derivative. The m.p. of 137° and the elementary analysis (75.89% C, 9.30% H, and 7.03% N) of the acetyl derivative corresponded to the figures for tertiary p-amyraniline [3].

The mixture of secondary amines (0.82 g) was freed of its residual aniline by zinc chloride, after which it was treated with p-toluene sulfochloride dissolved in pyridine. The resultant sulfamide had a m.p. of 83° after recrystallization, which is the melting point of 2-methyl-3-phenyl-p-toluenesulfaminobutane [4]. A small percentage of the secondary amines did not react with the sulfochloride. Upon nitrosation they yielded a compound that exhibited the qualitative reaction for N-nitrosamines, which we were unable to identify. The formation of N-nitrosamines leads us to assume that the mixture of secondary amines contained 2-methyl-2-phenylaminobutane.

The catalyst was prepared as follows; 200 g of sifted kaolin was boiled for 12 hours in 1500 ml of 25% sulfuric acid. After this boiling, the catalyst was washed free of the acid by decantation until its reaction was neutral, desiccated, and pressed into tablets.

LITERATURE CITED

- [1] K. Lavrovsky, A. Mikhnovskaya, and L. Omelchenko, *Dokl. USSR Acad. Sci.* **64**, 345 (1949).
- [2] French Patent 765450, Zbl., 1934, II, 2600; French Patent 850744, Zbl., 1940, I, 5375; British Patent 319205, Br. Chem. Ab., 1931, 105.
- [3] Beilstein, XII, 1179.
- [4] W. J. Hickinbottom, *J. Chem. Soc.*, 1935, 1279.

Received August 3, 1949.

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XVIII. SYNTHESIS AND PROPERTIES OF SOME QUINONE OXIDES

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As we know, quinones are formed in one of the initial stages of the oxidation of the ring groupings of aromatic compounds. Further oxidation of the quinones usually results, first, in the addition of an oxygen atom at the double bond of the quinone ring, yielding the respective oxides. The conditions governing the formation of quinone oxides, and their behavior toward oxidative and hydrolytic agents, were the subject of several of our previous reports on the oxidative-hydrolytic transformations of carbocyclic compounds [1-6]. The present report likewise deals with the problem of oxidizing quinones to the corresponding oxides, one of our basic objectives having been determining the feasibility of synthesizing quinone oxides of various types.

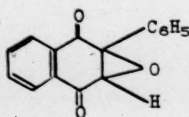
The oxides may be formed as intermediate or end products of the oxidation of quinones by all sorts of oxidants. It has been shown, for example, that oxides are formed as intermediate compounds in the reaction of *p*-benzoquinone with hydrogen peroxide in the presence of an alkali [7], in the reaction of alkaline solutions of permanganate or of hydrogen peroxide with 2-alkyl-substituted 3-hydroxy-1, 4-naphthoquinones [3,4], and apparently in the oxidation of boiling aqueous alkaline solutions of substituted 3-hydroxy-1, 4-naphthoquinones that contain chlorine, an amino group, or a pyridinium residue at the 2 atom by atmospheric oxygen [6]. As for the recovery of the oxides in the individual state, they have been secured up to now only from a limited group of quinones, viz: 1,4-naphthoquinone (by the action of salts of hypochlorous acid [8] or of hydrogen peroxide in the presence of soda [7], and substituted *p*-naphthoquinones that contain alkyl, alkenyl, aralkyl, or cyclohexyl radicals at the 2 or 2 and 3 positions (by the action of hydrogen peroxide in an aqueous solution of an alkali, or better yet, of soda [9]. Oxides of the naphthoquinones containing other radicals or substituents than those enumerated above attached to the quinone ring have not been described prior to this, as far as we know. Nor have any oxides of benzene quinones been known.

In the course of our research the problem arose of finding ways of synthesizing the oxides of various quinones that we needed in our investigation of the hydrolytic transformations of carbocyclic compounds in various stages of oxidation.

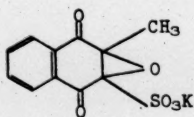
We found that the benzene and naphthalene quinones do not react with benzoyl hydrogen peroxide (Prilezhaev reaction), and that this reagent, which is employed fairly extensively in the synthesis of other types of oxides, could not be used for these compounds. The method of preparing oxides that involved the action of hydrogen peroxide upon the quinones in an aqueous soda solution proved to be more effective, though the field in which this method can be employed is likewise rather limited. We showed, for instance, that, in addition to the types of quinone oxides specified above, this method could be utilized to secure 2-phenyl-1,4-naphthoquinone oxide (I) and potassium 2-methyl-1,4-naphthoquinone-3-sulfonate (II), but not the oxides of 2-methyl-3-chloro- and 2-phenylamino-3-chloro-1, 4-naphthoquinone. Among the benzene quinones, the only oxide we were able to synthesize was 2-phenyl-1, 4-benzoquinone oxide (III),¹ and then only after substituting sodium bicarbonate for the soda. With 1,4-benzoquinone and 2-methyl-1,

¹) It should be noted that the location of the oxidic oxygen in the molecule of this compound has not been rigorously determined.

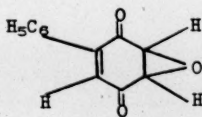
4-benzoquinone the reaction yielded merely the corresponding hydroquinones, while 2,5-diphenyl-1,4-benzoquinone did not react at all with a solution of hydrogen peroxide containing soda:



(I)



(II)



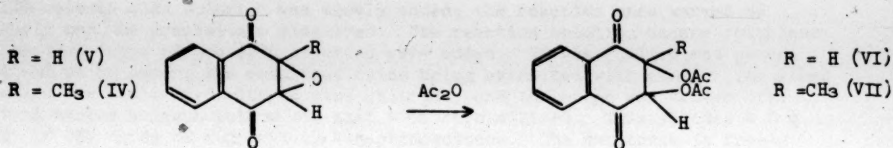
(III)

The synthesized oxides are white crystalline substances that dissolve fairly rapidly in aqueous sodium hydroxide, turning the solution red, though they are unaffected by aqueous solutions of soda or sodium bicarbonate, with the sole exception of the oxide of 2-phenyl-1,4-benzoquinone (III), which undergoes a change when reacted with a soda solution.

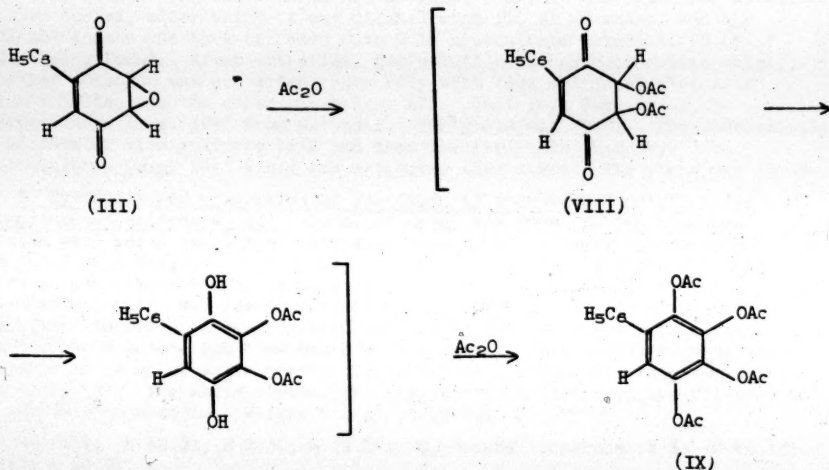
In one of our previous reports [2] we noted that the oxidic oxygen in the molecule of 2-methyl-1,4-naphthoquinone oxide (IV) possesses oxidizing properties; this oxide can, for example quantitatively oxidize monovalent negative iodine to free iodine or divalent iron to the trivalent. We were interested in finding out whether this is a characteristic feature of the other quinone oxides as well. In a study of the reactions of various oxides with potassium iodide, we found that all of them can oxidize monovalent negative iodine to free iodine under certain conditions, so that the ability to oxidize is a general property of quinone oxides. In contrast to the oxide of 2-methyl-1,4-naphthoquinone (IV), in which this reaction is quantitative (being accompanied by the reduction of the oxide to the respective quinone [2]), most of the other oxides we investigated possessed a much lower oxidizing ability, to be sure, it being found that other changes occurred alongside the reduction of the original oxides, such as hydration to the respective glycols, which were then dehydrated to monohydroxyquinones. Thus, when 2-phenyl-1,4-naphthoquinone oxide (I) was reacted with potassium iodide, the latter was oxidized to free iodine, only 80% of the oxide being reduced to 2-phenyl-1,4-naphthoquinone, some 15% of the oxide being converted (via the respective glycol) into 2-phenyl-3-hydroxy-1,4-naphthoquinone. A similar phenomenon is observed to occur with the oxide of 1,4-naphthoquinone (V), but in this case the oxidative-reducing transformations account for only 20%, the yield of the 2-hydroxy-1,4-naphthoquinone totaling 75%. The oxide of potassium 2-methyl-1,4-naphthoquinone-3-sulfonate (II) undergoes even more complex changes. When the latter is boiled in acetic acid solution with potassium iodide, the iodine that is formed does not exceed 20-25%, so that the original oxide not only oxidizes the potassium iodide, but also reacts with the resulting iodine, being converted into 2-methyl-3-hydroxy-1,4-naphthoquinone. As for 2-phenyl-1,4-benzoquinone oxide (III), it can oxidize potassium iodide quantitatively to free iodine at room temperature (in alcoholic solution containing hydrochloric acid).

As a rule, we were unable to isolate the glycols formed as intermediate products during the conversion of the oxides of *p*-naphthoquinones into monohydroxynaphthoquinones (*vide supra*, as well as [1, 2, 5]) in the pure state, as they exhibit a very high tendency to dehydration. Still, the glycols may sometimes be recovered as the corresponding azine derivatives [2, 10] in the hydration of the original oxides with an aqueous solution of *p*-phenylenediamine present. We have now discovered the possibility of securing still another type of derivatives of these glycols, *viz.* their esters, which are readily formed when quinone oxides are reacted with acetic anhydride in the presence of sulfuric acid. In the oxides

of 1, 4-naphthoquinone (V) and 2-methyl-1, 4-naphthoquinone (IV), this reaction takes place at room temperature, resulting in the formation of diacetyl derivatives of the respective glycols (VI) and (VII), which are fairly stable white crystalline substances, which are readily changed, to be sure, in the presence of alkali solutions (*vide infra*).



The reaction of the oxide of 2-phenyl-1, 4-benzoquinone (III) with acetic anhydride is somewhat different. Here the process does not come to a stop at the stage in which the diacetyl derivative (VIII) is formed, but goes further, finally resulting in the tetra-acetyl derivative (IX). The way in which the latter compound is formed may be pictured as follows:



In conclusion, we should like to point out that the properties of the esters of the glycols (VI) and (VII) we have synthesized leave no doubt as to their structure. When the first of these compounds, (VI), is heated with acetic anhydride and sodium acetate, it splits off acetic acid and is converted into 2-acetoxy-1, 4-naphthoquinone, while it is rapidly saponified and oxidized in an aqueous-alcoholic solution of alkali with atmospheric oxygen present, yielding 2, 3-dihydroxy-1, 4-naphthoquinone, as with the oxide (V) (*cf* [5]). As for Compound (VII), it is very easily saponified and dehydrated in an aqueous-alcoholic alkali solution, being converted, like the oxide (IV), into 2-methyl-3-hydroxy-1, 4-naphthoquinone (*cf* [1]).

EXPERIMENTAL¹

1. Synthesis and properties of the oxide of 2-phenyl-1, 4-naphthoquinone (I). 5 g of 2-phenyl-1, 4-naphthoquinone (m.p. 109° [11]) was heated in 125 ml of methanol until it dissolved and then cooled to 20°, after which 20 ml of 30% hydrogen peroxide was added and the mixture was vigorously stirred while 30 ml of 10% aqueous soda solution was slowly added; the reaction mass warmed up slightly and the precipitate dissolved. The reaction solution became colorless as the last drops of the soda solution were added. It was chilled and poured into 400 ml of water, the resultant oxide being extracted with ether. The ether solution was desiccated with calcium chloride, and the ether was driven off, leaving behind a light-yellow oil that soon crystallized. This yielded 4.0 g (75%) of the oxide of 2-phenyl-1, 4-naphthoquinone. The substance is freely soluble in most organic solvents. Recrystallization from methanol yielded white crystals with a m.p. of 63°.

Found %: C 76.59; H 3.75. $C_{16}H_{10}O_3$. Calculated %: C 76.80; H 4.00.

Investigation of the oxidizing ability of the oxide. A sample of the oxide (about 0.2 g) was dissolved in 45 ml of glacial acetic acid, and 0.5 g of potassium iodide was added. The solution turned brown at once; it was boiled for 45 minutes and then cooled, after which it was diluted with 150 ml of water, and the resultant iodine was back-titrated with 0.1N hyposulfate solution, 78.6% of iodine being found. After titration, the solution was extracted with ether, the ether solution was extracted repeatedly with soda and desiccated with sodium sulfate, and the ether was driven off. This left 2-phenyl-1, 4-naphthoquinone (m.p. 109° from alcohol). The yield was 79.5%. The soda solution was acidulated with sulfuric acid and then the 2-phenyl-3-hydroxy-1, 4-naphthoquinone (m.p. 146° [12]) was extracted with ether. The yield was 15.7%.

2. Synthesis and properties of the oxide of potassium 2-methyl-1, 4-naphthoquinone-3-sulfonate (II). 20 ml of water and 20 ml of 30% hydrogen peroxide were added to 10 g of potassium 2-methyl-1, 4-naphthoquinone-3-sulfonate. Then 17 ml of 30% aqueous potassium carbonate was gradually added with vigorous stirring, the reaction mass warming up slightly and the precipitate dissolving. The solution, which was nearly colorless, was rapidly chilled to 10°, and the precipitate thrown down was filtered out and washed, at first with a small amount of cold water, and then twice with acetone. The resultant oxide was dissolved in 10 ml of water previously heated to boiling, and then rapidly chilled to 10°. The white crystalline precipitate thrown down was filtered out and washed with acetone. Weight 5.2 g; yield 49%.

Found %: C 42.81; H 2.30; K 12.84. $C_{11}H_7O_6SK$. Calculated %: C 43.13; H 2.28; K 12.74.

Investigation of the oxidizing ability of the oxide. The reaction was carried out as described for Experiment 1. Percentage of iodine found: 22% and 25%. After titration was completed, the solution was extracted with ether, and the ether extract was in turn extracted repeatedly with a soda solution. The soda solution was acidified with sulfuric acid and extracted with ether, the extract being desiccated with sodium sulfate, and the ether then driven off. The residue consisted of 2-methyl-3-hydroxy-1, 4-naphthoquinone (m.p. 172° [14]; from methanol).

A more detailed study of this reaction disclosed that the oxide of potassium

¹ The analytical section of these investigations was done with the assistance of E. A. Ignatyeva, to whom we are deeply grateful.

2-methyl-1, 4-naphthoquinone-3-sulfonate not only could oxidize potassium iodide, but also could react with the iodine produced. For when this oxide was boiled for 45 minutes with a 0.1N solution of iodine in glacial acetic acid, it reduced the iodine and was quantitatively converted into 2-methyl-3-hydroxy-1, 4-naphthoquinone, which can be recovered from the solution by the method described above.

3. Synthesis and properties of the oxide of 2-phenyl-1, 4-benzoquinone (III).
1 g of 2-phenyl-1, 4-benzoquinone (m.p. 114° [15]) was heated in 6 ml of ethyl alcohol until it dissolved, after which the solution was cooled, and the resultant quinone precipitate was thoroughly triturated while still in the solution. Without interrupting the trituration of the reaction mixture, we then added 3 ml of 30% hydrogen peroxide and a solution of 0.4 g of sodium bicarbonate in 5 ml of water. The reaction solution turned dark red, while the precipitate gradually became lighter. The temperature of the reaction mass rose to 38-40° within 5-7 minutes. Then the mixture was chilled with ice, and the precipitate was filtered out and thoroughly washed with water until the reaction of the wash water was neutral. The precipitate (weighing 0.45 g) was dissolved by heating it in 25 ml of heptane, the solution being boiled with activated charcoal, filtered, and reduced to a volume of 7-9 ml. 0.2 g of yellow crystals with a m.p. of 105-111° was thrown down; these crystals were repeatedly recrystallized from a small amount of benzene. The resultant oxide was a white crystalline substance with a m.p. of 121.5-122.5°. Before being analyzed it was dried in vacuum at 100°. The substance is freely soluble in the usual organic solvents, with the exception of heptane, in which it is much less soluble.

Found %: C 71.96; H 4.17. $C_{12}H_8O_3$. Calculated %: C 72.00; H 4.00.

Investigation of the oxidizing ability of the oxide. A sample of the oxide (about 0.2 g) was dissolved in 20 ml of alcohol, and 20 ml of concentrated hydrochloric acid and 1 g of potassium iodide were added. Two hours later 100 ml of water was poured in, and the resulting iodine was back-titrated with a 0.1 hyposulfite solution. The iodine was produced quantitatively.

Acetylation of the oxide. 0.25 g of the oxide was dissolved in 5 ml of acetic anhydride and the solution was chilled, while 0.5 ml of concentrated H_2SO_4 was added. The reaction mixture turned yellow. Two hours later it was poured into 100 ml of water and stirred until all the acetic anhydride had decomposed; a white precipitate of the tetra-acetate (IX) was thrown down and filtered out. Weight 0.42 g; yield 87%. Recrystallization from alcohol yielded white needles with a m.p. of 175-176°. The substance was dried in vacuum at 100-110° before being analyzed.

Found %: C 62.28; H 4.79. $C_{20}H_{14}O_8$. Calculated %: C 62.17; H 4.63.

The number of acetyl groups was determined by dissolving a sample of the substance in a water-dioxane mixture and boiling the solution for 3 hours with concentrated phosphoric acid, after which the resulting acetic acid was driven off with steam and determined by titration with an alkali solution. This indicated that the number of acetyl groups was 3.9.

4. Properties of the oxide of 1, 4-naphthoquinone (V). Acetylating the oxide
0.6 g of the oxide was dissolved in a mixture of 15 ml of acetic anhydride and 1.5 ml of concentrated sulfuric acid. Within 3-5 minutes elongated white needles began to settle out of the solution, the reaction mass soon solidifying into a thick mass. The precipitated diacetate (VI) was filtered out and washed with ether, with a small amount of alcohol, and, lastly, with water. The filtrate was poured into 100 ml of water and stirred until all the

acetic anhydride had decomposed, a slight additional amount of the diacetate settling out. The resultant precipitates were combined and recrystallized from alcohol. The substance crystallized as white needles with a m.p. of 193-194°. Weight 0.7 g; yield 73%. It was dried in vacuum at 120° before being analyzed.

Found %: C 60.69; H 4.33. M 276 (in nitrobenzene). $C_{14}H_{12}O_5$.
Calculated %: C 60.87; H 4.33. M 276.

Properties of the diacetate (VI). a) 0.3 g of the diacetate synthesized above, 0.3 g of anhydrous sodium acetate, and 7.5 ml of acetic anhydride were heated to 100° for 1 hour. Then the reaction mass was cooled and poured into 100 ml of water, the whole being stirred until all the acetic anhydride decomposed. The light-yellow precipitate that was thrown down was filtered out. Weight 0.2 g; m.p. 128-129° (from alcohol). The substance fused at the same temperature when mixed with 2-acetoxy-1, 4-naphthoquinone [16].

b) 0.7 g of the diacetate was dissolved in 15 ml of a 10% alcoholic solution of potassium hydroxide, and a strong current of air was passed through the resultant blue solution for 5 minutes, after which the reaction mass was poured into 150 ml of water and acidified with sulfuric acid. The resultant precipitate was repeatedly extracted, together with the solution, with ether. Driving off the ether yielded a brick-red precipitate of 2, 3-dihydroxy-1, 4-naphthoquinone (isonaphthazarine). Weight 0.45 g (93%). M.p. 280-281° (from acetic acid).

Investigation of the oxidizing ability of the oxide. a) The reaction was carried out as described under Experiment 1. Per cent of iodine found: 53%.

b) A sample of the oxide of 1, 4-naphthoquinone [7] (about 0.2 g) was dissolved in 15 ml of alcohol, and 10 ml of concentrated hydrochloric acid and 0.5 g of potassium iodide were added, the solution immediately turning red-brown. The reaction mixture was heated to 70° for 15 minutes, cooled, and 150 ml of water was added. The resulting iodine was back-titrated with a 0.1N hyposulfite solution. Per cent of iodine found: 22.5%. After titration, the solution was extracted with ether, and the ether extract was in turn repeatedly extracted with a soda solution and desiccated with calcium chloride, after which the ether was driven off. This left 1, 4-naphthoquinone with a m.p. of 126-127° (from alcohol). Yield: 20%. After the soda solution had been acidified with sulfuric acid, the 2-hydroxy-1, 4-naphthoquinone (m.p. 190-191°) was extracted with ether. Yield: 75%.

5. Properties of the oxide of 2-methyl-1, 4-naphthoquinone (IV). Acetylating the oxide. 1 g of the oxide was dissolved in 5 ml of acetic anhydride, and 0.5 ml of concentrated sulfuric acid was added while the solution was water-cooled. The solution turned yellow. Two days later the reaction mass was poured into 150 ml of water and the mixture stirred until all the acetic anhydride had dissolved, after which the white precipitate of the diacetate (VII) was filtered out and twice recrystallized from alcohol. Weight 1.25 g (81%); m.p. 122-123°. The substance crystallized from alcohol as white needles.

Found %: C 61.91; H 4.92; M 290, 301. (in nitrobenzene and in dioxane). $C_{15}H_{14}O_5$. Calculated %: C 62.07; H 4.83. M 290.

Properties of the diacetate (VII). 1 g of the substance synthesized above was dissolved by heating it in 10 ml of alcohol, and after the solution had cooled, 1 ml of a 3% aqueous solution of sodium hydroxide was added. The reaction mixture instantly turned dark red. One to two minutes later 100 ml of water was poured into the solution, which was then acidulated with sulfuric

acid. The yellow precipitate that was thrown down was not filtered out, but the whole was extracted with ether, the ether solution yielding 0.56 g of 2-methyl-3-hydroxy-1, 4-naphthoquinone, with a m.p. of 172°. Yield: 90%.

SUMMARY

Several quinone oxides have been synthesized and some of their properties studied: the oxidizing ability of the oxides, and the possibility of converting them into esters of the respective glycols.

LITERATURE CITED

- [1] L. A. Shchukina, A. P. Kondratyeva, and M. M. Shemyakin, Jour. Gen. Chem. **19**, 183 (1949). ¹⁾
- [2] L. A. Shchukina and M. M. Shemyakin, Jour. Gen. Chem. **19**, 193 (1949). ²⁾
- [3] L. A. Shchukina, A. P. Kondratyeva, and M. M. Shemyakin, Jour. Gen. Chem. **19**, 468 (1949). ³⁾
- [4] L. A. Shchukina, Yu. B. Shvetsov, and M. M. Shemyakin, Jour. Gen. Chem. **21**, 346 (1951). ⁴⁾
- [5] L. A. Shchukina, A. S. Khokhlov, and M. M. Shemyakin, Jour. Gen. Chem. **21**, 917 (1951). ⁵⁾
- [6] D. P. Vitkovsky and M. M. Shemyakin, Jour. Gen. Chem. **21**, 1033 (1951). ⁶⁾
- [7] E. Weitz, H. Schobbert, H. Spibert, Ber., **68**, 1163 (1935).
- [8] Th. Zincke, Ber., **25**, 3599 (1892); L. Fieser, J. Am. Chem. Soc. **70** 3165 (1948).
- [9] J. Lugs, A. Macbeth, F. Winzer, J. Chem. Soc., 1934, 1537;
J. Madinaveitia, Zbl., 1934, II, 244; L. Fieser et al., J. Am. Chem. Soc. **61**, 3216 (1939), **62**, 2866 (1940), **70**, 3165 (1948).
- [10] Th. Zincke, Ber., **25**, 3599 (1892); Th. Zincke, P. Weigand, Ann., **286**, 56 (1895).
- [11] A. Breuer, Th. Zincke, Ber., **11**, 1114 (1878).
- [12] Th. Zincke, A. Breuer, Ann., **11**, 31 (1874).
- [13] D. A. Blovvar, L. A. Shchukina, A. S. Chernyshev, N. G. Semenova, and M. M. Shemyakin, Jour. Gen. Chem. **19**, 183 (1949).
- [14] L. Fieser, J. Am. Chem. Soc., **70**, 3165 (1948).
- [15] D. Kvalnes, J. Am. Chem. Soc., **70**, 3165 (1948).
- [16] J. Thiele, E. Winter, Ann., **211**, 217 (1902).

Received October 14, 1952

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¹⁾ See Consultants Bureau English translation, p. 165.

²⁾ As above, p. 175. ³⁾ As above, p. 419. ⁴⁾ As above, p. 381.

⁵⁾ As above, p. 1005. ⁶⁾ As above, p. 1151.

OXIDATIVE AND OXIDATIVE-HYDROLYTIC TRANSFORMATIONS OF ORGANIC MOLECULES

XIX. THE RELATIONSHIP BETWEEN THE DEGREE OF OXIDATION OF CARBOCYCLIC COMPOUNDS AND THE ABILITY OF THEIR RINGS TO BE CLEAVED HYDROLYTICALLY

M. M. Shemyakin, L. A. Shchukina, Yu. B. Shvetsov, D. P. Vitkovsky, and
A. S. Khokhlov

In recent years we have undertaken a systematic investigation of the reactions that take place when oxidizing and hydrolyzing agents act upon^{*} organic substances, either simultaneously or consecutively. These reactions, which often result in the cleavage of the carbon bonds in the original or intermediate molecules during certain stages, are of interest inasmuch as their study has made possible an approach from a new angle to the essential nature of one of the major types of oxidative transformations of organic substances: namely, their oxidative cleavage.

There is no doubt that all biochemical oxidation reactions, we well as the overwhelming majority of chemical oxidations, occur under conditions that do not exclude the possibility of hydrolytic cleavage of the carbon bonds. But up to recently the processes involved in the oxidative cleavage of organic molecules have usually been regarded as the result of the action of the oxidants alone, insufficient attention being paid to the part played by the reaction medium. The onesidedness of this approach compelled us to make a special study of the problem, we began our investigations with the quinones, later extending them to other types of carbocyclic and, partly, to acyclic compounds (cf [1-18]).

A comparison of the results of these researches with the earlier data led us to conclude, from the very start [1], that the oxidative cleavage of carbon bonds in the presence of hydrolytic agents must be regarded as oxidative-hydrolytic rather than as purely oxidative. In fact, we found that the action of oxidants upon the original compounds under conditions that excluded any hydrolysis of the carbon bonds or did not promote this hydrolysis sufficiently, most often results merely in the entrance of oxygen-containing substituents into the molecule, without involving cleavage of the carbon bonds.¹ The result of oxidative processes of this sort in molecules that still retained their original carbon skeleton, however, was an accumulation of oxygen-containing groups, which, at certain stages of oxidation, provided the structural prerequisites for a purely hydrolytic cleavage of the carbon bonds. Thus the oxidizing agents in many instances are unable to cleave the carbon bonds, but they predetermine the subsequent cleavage of these bonds by hydrolytic agents, so that transformations of this sort must be regarded as oxidative-hydrolytic.

For a correct understanding of the oxidative-hydrolytic transformations of organic compounds it is of basic importance to know the following:

¹ An exception is represented by the oxidation reactions that result in the formation of: 1) compounds that are thermally unstable at the given temperature; and 2) peroxide compounds (that may have the structure, possibly, of biradicals), whose further decomposition apparently involves the formation of free radicals as intermediate products.

1) Why can preliminary oxidation of molecules affect the subsequent cleavage of their carbon bonds?

2) What is the relationship between the degree of oxidation of molecules and the ability of their carbon bonds to undergo hydrolytic cleavage?

The answers to these questions have been the major objective of our researches in this field during the past few years, carried on chiefly with carbocyclic compounds.

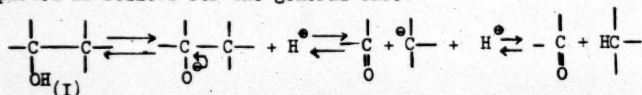
Inasmuch as the oxidative-hydrolytic cleavage of the carbon bonds is the result of the simultaneous or consecutive action of oxidizing and hydrolyzing agents upon organic molecules, study of such reactions is usually feasible only when the action of each of these two factors can be investigated separately. For that reason the following methods of attack proved to be highly advantageous in shedding light upon the individual stages of oxidative-hydrolytic transformations and upon the nature of the phenomenon as a whole:

1) Step-by-step oxidation of the original substances with no hydrolyzing agents present.

2) Investigating the processes involved in the hydrolytic cleavage of carbon bonds in representative compounds of each stage of oxidation of the original compound when no oxidants (especially atmospheric oxygen) are present.

3) Cleaving the molecules hydrolytically in dilute aqueous solutions at constant values of the medium pH, which are as close to 7 as possible.¹

These research procedures, as well as the methods we have developed for isolating and separating the resultant substances [1-8] made it possible to ascertain the nature and the mechanism of the hydrolytic cleavage of carbon bonds in various types of carbocyclic compounds that had previously been oxidized. We found [1] that reactions of this sort may occur, in principle, with all compounds that already contain or may acquire an atom grouping of Type (I);² while, as for the cleavage process itself, its mechanism may be depicted as follows for the general case:



At the same time we demonstrated that, in accordance with the rules that had been previously derived by one of the present authors (M. M. Shemyakin [19]) for the reactions involved in the hydrolytic cleavage of carbon bonds in general, the occurrence of these transformations in carbocyclic compounds depends both upon the external conditions (pH of the medium and temperature) under which the reactions are carried out and upon the structure of the compounds exposed to the action of the hydrolytic agents, the carbon bonds of

²) This grouping is often formed, for example, as the result [1, 3-8, 11-17] of the hydration of the $>C=C<$ or $>C=O$ double bond, as well as in the addition of elements of ammonia at the carbonyl group [10].

¹) The latter specification is required because the initial cleavage products tend very often to undergo further changes during the very process of their formation.

the rings proving to be readily cleavable (as might have been expected) only when the substituents in the molecules can polarize these bonds sufficiently, owing to their nature, their number, and their position.

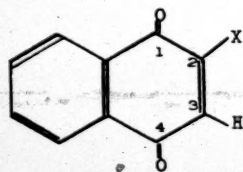
The correctness of these assertions, set forth in our first report [1], was subsequently borne out by our later researches [2-18] on the hydrolytic and oxidative-hydrolytic transformations of carbocyclic compounds in various stages of oxidation. In our previous reports we have been able to give no more than a partial discussion of the nature and cause of the relationship existing between the degree of oxidation of carbocyclic compounds and the ability of the carbon bonds in their rings to be cleaved hydrolytically, owing to the sparseness of the experimental data at our disposal. The material now available, however, enables us to provide a definite answer to that question.

As we have said above, the action of oxidizing agents upon carbocyclic compounds (under conditions that exclude the possibility of any hydrolysis of the carbon bonds or do not favor such hydrolysis) results most often in the entrance of various oxygen-containing substituents into the original molecules. The presence of the latter in the oxidized molecules, which still retain their original carbon skeletons, cannot help affecting the polarization of the carbon bonds in these molecules in many cases and, hence, affecting their ability to undergo hydrolytic cleavage. This makes it clear why the action of oxidants upon carbocyclic compounds usually exerts extremely great influence upon the hydrolytic cleavage of their rings during certain stages of their oxidation. It also explains the relationship existing between the degree of oxidation of the molecules and the ability of the latter's carbon bonds to be cleaved hydrolytically. This relationship may be stated as follows for the general case: the more strongly the oxygen-containing substituents that enter a molecule as a result of the action of an oxidant polarize the carbon bonds subject to hydrolytic cleavage, the more readily will the latter process occur (provided, of course, the carbon bonds are polarized as depicted above for compounds of the general type (I); cf [19-24]).

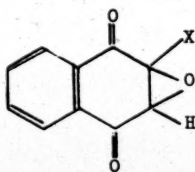
This conclusion, in turn, has several corollaries that are fairly evident, since the hydrolytic cleavage of the carbon bonds in carbocyclic compounds obey the general rules established earlier [19-24] for analogous transformations in other types of organic compounds. Thus, it must be thought that far from every oxygen-containing substituent that enters a molecule will necessarily and sufficiently polarize the carbon bonds, thus facilitating their cleavage in the presence of hydrolyzing agents. Whence it could have been foreseen (cf Par. 4 of Report I [1] as well as [19]) that at times the prior action of oxidants will have no effect at all upon the hydrolytic cleavage of the carbon bonds of carbocyclic compounds; in some cases it might even be expected that introducing oxygen-containing groups will hinder such processes. There was no doubt, however, that at certain stages of oxidation the entrance of oxygen-containing substituents into a molecule could greatly facilitate the hydrolytic cleavage of the carbon bonds, inasmuch as considerable preliminary data had indicated that the higher the degree of oxidation of carbocyclic compounds (cf Par. 3 of Report I [1]), the easier it was for this process to take place. Lastly, it was apparent that the hydrolytic cleavage of rings must depend upon the presence of the substituents existing in the original molecules and retained in the oxidized ones, in addition to the presence of the substituents introduced during oxidation.

All these problems required appropriate experimental research, of course, which we undertook. Our data (cf [2-18]) now justify the assertion that both the general formulation of the relationship we have discovered, set forth above, and the conclusions derived therefrom are correct.

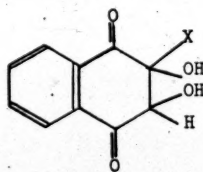
In fact, the results of our research on the conditions and nature of the hydrolytic cleavage of carbocyclic compounds in various stages of oxidation indicate beyond any doubt that this process is directly related to the polarization of the carbon bonds undergoing cleavage, this polarization, in turn, depending upon the nature, number, and position of the substituents either present in the original molecules already or introduced during their oxidation. The oxidation of naphthalene or of its respective derivatives to p-naphthoquinone does not result in the establishment of the structural prerequisites within the molecule that are adequate to promote the cleavage of the ring when hydrolyzing agents are present. This is due to the fact that the carbonyl groups at the 1 and 4 positions in p-naphthoquinone cannot polarize the bonds between the 2 and 3 carbon atoms [which must first be hydrated and then ruptured (cf [1])]; this is readily seen when we consider the structure of such compounds from the standpoint of modern concepts of the interactions of atoms and of groups of atoms within molecules. That is why 1,4-naphthoquinone (II) cannot be cleaved hydrolytically as such, but only after a preliminary oxidation [2]; the same is true of 2-methyl-(III) and 2-ethyl-1,4-naphthoquinone (IV) [2], because, as we know, alkyl groups are unable to polarize carbon bonds appreciably.¹ Nor does further oxidation of these p-quinones to oxides or hydration of the latter to the corresponding glycols yield compounds that tend to be cleaved in the presence of hydrolyzing agents, since the entrance of oxidic oxygen or of two hydroxyl groups at the 2 and 3 positions in the quinone molecule naturally cannot aid in polarizing the bond between these carbon atoms. In fact, the oxides (V) and (VI) and the corresponding glycols (VII) and (VIII), like the original quinones (II) and (III), cannot be cleaved hydrolytically without prior change of their molecules [4, 5, 15]. These examples indicate, therefore, that the action of oxidants upon carbocyclic compounds may sometimes fail to yield substances that are more readily cleaved than the original compounds. In the instances considered above, the reason for this is the fact that the entering oxygen-containing substituents were unable to polarize the bond between the 2 and 3 carbon atoms in the ring.



(II) X = H
(III) X = CH₃
(IV) X = C₂H₅

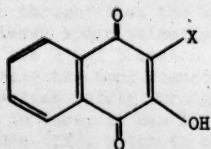


(V) X = H
(VI) X = CH₃

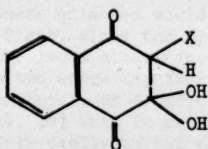


(VII) X = H
(VIII) X = CH₃

¹ We have observed that the methyl group has no perceptible effect upon the hydrolytic cleavage of carbon bonds in other cases as well, such as the oxides of p-naphthoquinones, the glycols corresponding to these oxides, and the monohydroxy-p-naphthoquinones [3-5, 14, 15].



(IX) X = H
(X) X = CH₃

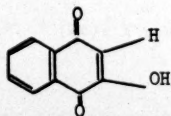


(XI) X = H
(XII) X = CH₃

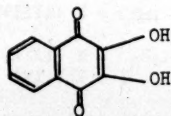
A wholly different result is observed, however, when a hydroxyl group is added to the molecule of some p-quinones at the 3 position. Such monohydroxy-naphthoquinones as (IX) and (X) can be readily hydrated at the double bond (which is strongly polarized by the hydroxyl group), being converted into the respective hydration products (XI) and (XII); in the latter compounds the presence of two hydroxyl groups at the 3 position polarizes the single bond between the 2 and 3 atoms very strongly as well, making it unstable in the presence of hydrolyzing agents. Hence, the monohydroxynaphthoquinones (IX) and (X) [in contrast to the p-quinones (II) and (III) and to the corresponding oxides and glycols] undergo purely hydrolytic cleavage fairly easily when their aqueous solutions, which have a pH somewhat higher than 7, are boiled, being transformed into o-acetyl- and o-propionylphenylglyoxylic acids [3, 14].¹

These examples indicate the importance of the nature, number, and importance of the oxygen-containing substituents that enter a molecule in judging their effect upon the hydrolytic cleavability of the ring carbon bonds.

In this connection it is also of some interest to compare the properties of the glycols (VII) and (VIII) with those of the isomeric compounds (XI) and (XII), the only structure difference between the two being the position of the hydroxyl groups. As we have pointed out above, it is this very difference that makes the former compounds unable to undergo hydrolytic cleavage under conditions in which the second group is cleaved rather readily, inasmuch as it is only in the latter that the hydroxyl groups polarize the bond between the 2 and 3 carbon atoms. Another instance of this is the differing resistance to hydrolysis of the rings in 3-hydroxy-1,4-naphthoquinone (IX) and 2,3-dihydroxy-1,4-naphthoquinone (iso-naphthazarine) (XIII):



(IX)

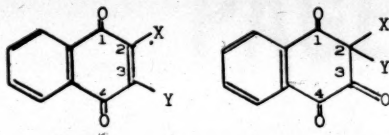


(XIII)

¹) The ability to be hydrolytically cleaved with ease is characteristic not only of the naphthalene monohydroxyquinones discussed above, but likewise of the similarly constructed monohydroxy-p-quinones of the benzene series (L. A. Shchukina's findings) and of phenanthrene (L. Fieser's findings [32]).

it should be thought that the second of these quinones would be incomparably harder to cleave hydrolytically than the first, since the hydroxyl groups attached to the 2 and 3 carbon atoms of the isonaphthazarine molecule (XIII) cannot polarize the bond connecting these two atoms together, whereas the same bond is polarized fairly strongly in the molecule of 3-hydroxy-1,4-naphthoquinone (IX). And, in fact, it has been shown [14, 16] that in contrast to 3-hydroxy-1,4-naphthoquinone (IX), which is cleaved fairly easily by hydrolyzing agents, isonaphthazarine (XIII) cannot be cleaved hydrolytically, even under quite severe conditions. A comparison of the properties of these two quinones is also interesting because here we have the rather rare case where an increase in the number of oxygen-containing substituents in the molecule not only does not promote, but, on the contrary, greatly hampers the hydrolytic cleavage of the carbon bonds.

In the molecule of 3-hydroxy-1,4-naphthoquinone (IX) the bond between the 2 and 3 carbon atoms may be depolarized by introducing at the 2 position, in addition to a hydroxyl group, other substituents, such as an amino group, which we know exerts a polarizing effect that parallels the action of the hydroxyl group, though of different strength. We therefore were led to believe that not only isonaphthazarine (XIII) and 2-amino-3-hydroxy-1,4-naphthoquinone (XIV), but 2-pyridinium-3-hydroxy-1,4-naphthoquinone betaine (XV) as well, would resist hydrolytic agents effectively, in sharp contrast to the behavior of 3-hydroxy-1,4-naphthoquinone (IX). This supposition proved to be correct - it was found [12, 17] that, like isonaphthazarine (XIII), the compound (XIV) is hard to cleave hydrolytically in general; as for the quinone (XV), it can be cleaved, to be sure, but the conditions required are much more severe than for 3-hydroxy-1,4-naphthoquinone (IX).¹ Hence, the effect of oxygen-containing groups upon the cleavage of the carbon bonds in carbocyclic compounds is fully analogous to that of other kinds of substituents.



(XIII): X = OH; Y = OH (XVI): X = CH₃; Y = OH

(XIV): X = NH₂; Y = OH (XVII): X = CH₃; Y = OAc

(XV): X = NC₅H₅; Y = O (XVIII): X = CH₃; Y = Cl

(XIX): X = C₅H₅NCl; Y = Cl

(XX): X + Y = O

Relationships that are quite similar to those just discussed are also found to prevail when another carbonyl group is introduced into the p-quinone ring. The addition of a third carbonyl ring usually makes the resulting substance highly unstable in hydrolyzing agents. The reason for this is the well-known ability of carbonyl groups to polarize carbon bonds strongly; the simultaneous presence of three carbonyl groups in the ring is likewise of considerable importance. We have shown, for example [6-8, 11, 13], that the triketones (XVI) - (XIX) cannot only be readily hydrated at the double bond of the carbonyl group at the 3 position, but that they then undergo hydrolytic cleavage of the bond between the 2 and 3

¹ Cf [12] for the structure of the products of the hydrolytic cleavage of the quinone (XV).

carbon atoms in their rings.¹ The similarly constructed bicyclic triketones that have two halogen atoms attached to the second carbon atom in the ring possess the same properties [25-29]. It must be stressed, however, that although all these triketones are cleaved hydrolytically with great ease, the conditions under which this process can take place are largely governed by the nature of the substituents attached to the 2 carbon atom. In the hydrated triketone (XIX), for instance, the presence of a chlorine atom and a pyridinium group polarizes the bond between the 2 and 3 carbon atoms so strongly that the compound is cleaved in an aqueous solution even without heating [13]. In the hydrated triketones (XVI) - (XVIII) this bond is less highly polarized, of course, so that the aqueous solutions of these compounds have to be heated to cleave this bond hydrolytically [6-8, 11].² The bond between the 2 and 3 carbon atoms must be even less polarized in the hydrated triketones (XI) and (XII) produced by hydrating the hydroxynaphthoquinones (IX) and (X); accordingly, the hydrated forms of these quinones can be easily cleaved only when they are boiled in aqueous solutions having a pH in excess of 7 (see above for details, as well as [9, 14]). Thus, in this series of carbocyclic compounds, as in those discussed previously, the hydrolytic cleavage of the carbon bonds depends upon the nature, number, and position of the oxygen-containing radicals and of the other substituents attached to the molecule; in the cyclic triketones, however, the carbonyl groups play the predominant role.

It was fairly obvious that the entrance of an even larger number of carbonyl groups into the molecules of carbocyclic compounds (as the result of oxidation or in other ways) ought to yield compounds that are particularly subject to hydrolytic cleavage. We might expect, therefore, that the ring of the tetraketone (XX) would be cleaved with very great ease, since the hydration of the carbonyl group at the 2 or 3 position ought to polarize the bond between the 2 and 3 carbon atoms very strongly, owing to the presence of two carbonyl groups in the 3,4 or 1,2 positions. This assumption was confirmed experimentally [16]; it was found that the tetraketone (XX) is cleaved very rapidly when heated in aqueous solution, this process occurring almost instantaneously, even in the cold, at a pH in excess of 7.

Similar behavior is exhibited by polycarbonyl compounds belonging to other classes of carbocyclic or aliphatic-aromatic compounds: orthopyruvylphenylglyoxylic acid [6]; hydrated hexaketocyclohexane (triquinoyl) [30]; 1,2,3-triketointhane monohydrate (ninhydrin) [16]; and 1,4,9,10-anthradiquinone [31], all of which are extremely unstable in the presence of hydrolyzing agents, though they are highly stable compounds when such agents are absent, resisting heat and the action of oxidants, for example. Hence, the presence of three, four, and more carbonyl groups in a molecule greatly facilitates the hydrolytic cleavage of the carbon bonds.

The foregoing comparison of the factual data with the structure of various types of carbocyclic compounds indicates that the assertions made in this paper regarding the cause and the nature of the relationships prevailing between the degree of oxidation of molecules and the ability of their carbon bonds to be cleaved hydrolytically are actually correct. It is beyond any doubt that the

1) Cf [6-8, 11, 13] for the structure of the primary cleavage products of the triketones (XVI) - (XIX).

2) It is worthy of note that the bond between the 2 and 3 carbon atoms in the triketone (XVIII) can be ammonolyzed as well as hydrolyzed [10].

action of oxidizing agents upon the molecules can affect the hydrolytic cleavage of their carbon bonds only when the oxygen-containing substituents entering the molecule can exert a perceptible influence upon the polarization of these carbon bonds. This is precisely why the transition from *p*-quinones to their oxides, which are ordinarily formed as the initial oxidation products of the *p*-quinones with various oxidants,¹ as well as the conversion of the quinone oxides into the corresponding glycols, is not enough to facilitate the cleavage of the carbon bonds of their rings by hydrolyzing agents [4, 15]. However, the monohydroxyquinones formed by the dehydration of these glycols, which, like the oxides and the glycols, must be classed as the first stages of oxidation of the *p*-quinones, are readily cleaved hydrolytically in many cases [3, 14, 32], because their ring carbon bonds can be very highly polarized by the hydroxyl group.² Hence, whenever the oxides formed during the oxidation of the original quinones are converted into monohydroxyquinones via the glycols, their molecules may acquire the structural prerequisites to facilitate the ensuing hydrolytic cleavage of the ring carbon bonds. If, for whatever reason, no monohydroxyquinones are formed, (or they are cleaved under extremely severe conditions), auxiliary action of oxidizing agents is required to produce more readily cleaved compounds: oxides of the monohydroxyquinones, hydroxytriketones, tetraketones, etc. [4-6, 8, 11, 15-17]. It is worthy of note in this connection that partially oxidized carbocyclic compounds, such as the glycols (VII) and (VIII) are often highly susceptible to further oxidation, owing to their structural peculiarities, this taking place even with such weak oxidants as atmospheric oxygen [4, 5, 15-17]. Moreover, in some instances (which are rather rare, to be sure), the transition to the next stage of oxidation may not result in the formation of compounds that are readily cleaved by hydrolyzing agents. Highly significant in this respect is, for example, the behavior of the glycols (VII) and (VIII). In fact, though oxidizing the latter of the two yields the hydroxytriketone (XVI), which can be cleaved with extreme ease to *o*-lactylphenylglyoxylic acid, even by boiling in water [4, 5, 8], oxidation of the glycol (VII) yields isonaphthazarine (XIII), which exhibits absolutely no tendency toward hydrolytic cleavage, owing to its structural features (*vide supra*) [15, 16]. In this case even greater oxidation of the molecule is required for cleavage, namely: the conversion of the isonaphthazarine (XIII) into the tetraketone (XX), the ring of which is highly unstable in the presence of hydrolyzing agents (*cf* [16], as well as the foregoing).

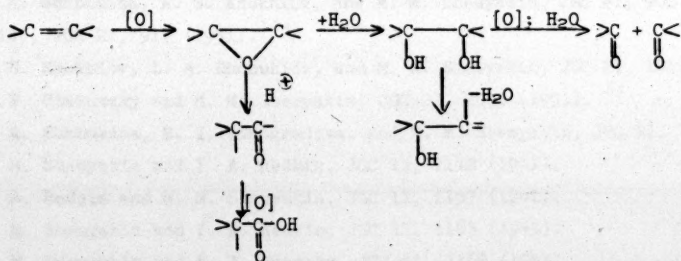
Thus, although the entrance of oxygen-containing substituents does not promote or even hinders the hydrolytic cleavage of the carbon bonds, further oxidation of the molecules to higher stages results, in certain stages, in the formation of compounds whose carbon bonds can be cleaved with great ease. Hence, the assertion made earlier [1] that increasing the degree of oxidation of the rings facilitates their subsequent hydrolytic cleavage holds good for an extremely broad range of carbocyclic compounds; it also applies, evidently, to other types of organic substances. It should, however, be borne in mind that departures from this rule may occur at some stages of oxidation of carbocyclic compounds, which may be foreseen in advance by applying the rule [19] that was derived for the hydrolytic cleavage of carbon bonds in general.

1) Especially atmospheric oxygen, hydrogen peroxide, and potassium permanganate [4, 6, 11, 15, 17, 18].

2) Moreover, some monohydroxyquinones cannot be cleaved hydrolytically or require extremely severe conditions for their cleavage, owing to the presence of still other substituents in their molecules (see above, as well as [12, 16, 17]).

In conclusion, it should be stressed that it is advisable to keep the concepts we have elaborated concerning the oxidative-hydrolytic transformations of organic substances in mind in any study of the oxidation reactions of acyclic as well as carbocyclic compounds, inasmuch as the correctness of these concepts has begun of late to be corroborated in such reactions as the oxidation of olefins, for example.

In fact, in accordance with our views, A. Byers and W. Hickinbottom have recently shown [33] that the first stage in the oxidation of olefins by organic per acids and by chromic anhydride or chromic acid is the formation of the respective oxides. When the reaction is carried out with no water present, the process comes to a stop at this stage, inasmuch as the oxides of unsaturated compounds, as might have been expected, cannot be oxidized further without undergoing prior changes (hydration, isomerization, etc.). It was found, for example, that the oxides resist the action of organic per acids, chromic anhydride, and potassium permanganate. Hence, the action of nothing but oxidizing agents upon olefins merely results in entrance of oxygen-containing substituents into their molecules, without cleaving their carbon bonds (cf footnote to P. 1831). The state of affairs is quite different, however, when the oxidation of the original olefins and the isolation of the oxidation products are carried out in the presence of water, especially when acids or alkalis are also present. In all such cases the oxides initially formed may be hydrated to glycols, isomerized to aldehydes, or undergo other transformations (cf [33] for details); some of the substances formed secondarily proving, in turn, to be capable of further oxidation. That is why the process does not stop at the stage in which oxides are formed when the reactions are carried out under such conditions, but continues much further, the end products usually containing, in addition to the normal products of olefin cleavage at the double bond, so-called anomalous oxidation products: unsaturated alcohols, carboxylic acids, and other substances that contain as many carbon atoms as the molecules of the original hydrocarbons. The causes of the formation of these substances, and the methods involved, which have remained unclear up to very recently, are now beginning to be elucidated, thanks to the fact that the end product of oxidative transformations has begun to be regarded [33] as the result of the action of the reaction medium as well as the oxidizing agent upon the initial and the intermediate molecules:



The examples we have discussed are clear enough proof that the concepts we have developed concerning the oxidative-hydrolytic transformations of organic molecules may be extremely useful in shedding light upon the mechanism involved in many kinds of oxidative reactions.

SUMMARY

The causes and nature of the relationship between the degree of oxidation of carbocyclic compounds and the ability of their ring carbon bonds to be cleaved hydrolytically have been elucidated.

It has been shown that it is advisable to keep the concepts set forth on the oxidative-hydrolytic transformations of organic molecules in mind when investigating the oxidation reactions of carbocyclic and acyclic compounds.

LITERATURE CITED

- [1] M. M. Shemyakin and L. A. Shchukina, JGC* 18, 1925 (1948).
- [2] L. A. Shchukina, A. P. Kondratyeva, and M. M. Shemyakin, JGC 18, 1945 (1948).
- [3] L. A. Shchukina, A. P. Kondratyeva, and M. M. Shemyakin, JGC 18, 2121, (1948).
- [4] Ibid., JGC 19, 183 (1949). ¹⁾
- [5] L. A. Shchukina and M. M. Shemyakin, JGC 19, 193 (1949). ²⁾
- [6] L. A. Shchukina, A. P. Kondratyeva, and M. M. Shemyakin, JGC 19, 468 (1949). ³⁾
- [7] Yu. B. Shvetsov and M. M. Shemyakin, JGC 19, 480 (1949). ⁴⁾
- [8] Yu. B. Shvetsov, L. A. Shchukina, and M. M. Shemyakin, JGC 19, 498 (1949). ⁵⁾
- [9] E. I. Vinogradova, Yu. B. Shvetsov, and M. M. Shemyakin, JGC 19, 507 (1949). ⁶⁾
- [10] Yu. B. Shvetsov, I. A. Redkin, and M. M. Shemyakin, JGC 21, 339 (1951). ⁷⁾
- [11] L. A. Shchukina, Yu. B. Shvetsov, and M. M. Shemyakin, JGC 21, 346 (1951). ⁸⁾
- [12] D. P. Vitkovsky and M. M. Shemyakin, JGC 21, 540 (1951). ⁹⁾
- [13] D. P. Vitkovsky and M. M. Shemyakin, JGC 21, 547 (1951). ¹⁰⁾
- [14] L. A. Shchukina, A. S. Khokhlov, and M. M. Shemyakin, JGC 21, 908 (1951). ¹¹⁾
- [15] Ibid., JGC 21, 917 (1951). ¹²⁾
- [16] A. S. Khokhlov, L. A. Shchukina, and M. M. Shemyakin, JGC 21, 1016 (1951). ¹³⁾
- [17] D. P. Vitkovsky and M. M. Shemyakin, JGC 21, 1033 (1951). ¹⁴⁾
- [18] L. A. Shchukina, E. I. Vinogradova, and M. M. Shemyakin, JGC 21, 1669 (1951). ¹⁵⁾
- [19] M. M. Shemyakin and I. A. Redkin, JGC 11, 1142 (1941).
- [20] I. A. Redkin and M. M. Shemyakin, JGC 11, 1157 (1941).
- [21] M. M. Shemyakin and I. A. Redkin, JGC 11, 1163 (1941).
- [22] M. M. Shemyakin and N. I. Oransky, JGC 11, 1169 (1941).
- [23] I. A. Redkin and M. M. Shemyakin, JGC 11, 1175 (1941).
- [24] M. M. Shemyakin and N. I. Oransky, JGC 13, 175 (1943).
- [25] Th. Zincke, E. Winzheimer, Ann., 290, 321 (1896).
- [26] Th. Zincke, B. Francke, Ann., 293, 120 (1896).

*All references indicated as JGC are to the Journal of General Chemistry of the USSR. See following page for the corresponding pagination of the English translation.

- [27] Th. Zincke, B. Francke, Ber., 29, 965 (1896).
[28] Th. Zincke, C. Gerland, Ber., 20, 3216 (1887).
[29] Th. Zincke, G. Gerland, Ber., 21, 2379 (1888).
[30] J. Houben. Methods of Organic Chemistry, Vol. III, 2, 213 (Russ.ed.)
[31] O. Dimroth, E. Schultze, Ann., 411, 345 (1916).
[32] L. Fieser, J. Am. Chem. Soc., 51, 940, 1896 (1929).
[33] A. Byers, W. J. Hickinbottom, J. Chem. Soc., 1948, 285, 1328, 1331, 1334; Nature, 160, 402 (1947).

Received October 14, 1949.

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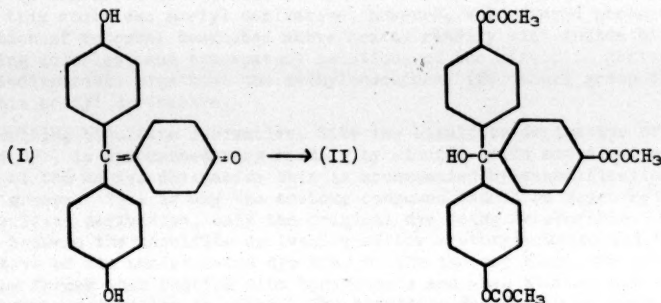
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- 1) See Consultants Bureau English translation, p. 165.
2) As above, p. 175.
3) As above, p. 419.
4) As above, p. 431.
5) As above, p. 447.
6) As above, p. 457.
7) As above, p. 373.
8) As above, p. 381.
9) As above, p. 597.
10) As above, p. 607.
11) As above, p. 997.
12) As above, p. 1005.
13) As above, p. 1113.
14) As above, p. 1131.
15) As above, p. 1831.

RESEARCH ON HYDROXYFUCHSONE DYES

XV. ACETOXYFUCHSONES

I. S. Ioffe

When hydroxyfuchsones dyes are acetylated, it is not only the hydroxy group that can react with the acetylating agent, but the methylenequinone group of the dye as well. These processes have not been successfully separated up to the present time, their parallel course usually yielding colorless products of the exhaustive acetylation of the hydroxyfuchsones dyes with a polyacetoxytriarylcarbinol structure [1]. Long ago [2] 4,4',4''-triacetoxytriphenylcarbinol (II) was synthesized from aurin (I). We have secured the corresponding acetoxytriarylcarbinols from other hydroxyfuchsones dyes as well [1].



Not so long ago we noticed, however, that the hydroxy groups of hydroxyfuchsones dyes react with acetylating agents faster than did the methylenequinone group. Under certain, milder conditions we were able to secure colored acetylation products containing the methylenequinone group unchanged. These acetoxyfuchsones, undescribed previously, were acetylated further, though under more severe conditions, being converted into colorless exhaustive-acetylation products whose structure was that of a polyacetoxytriarylcarbinol.

The most striking results were secured in the acetylation of rubrocol, 3,3',3''-trimethoxy-4,4'-dihydroxyfuchsones (III). The usual acetylation of this hydroxyfuchsones dye by heating it with acetic anhydride yielded the colorless 3,3',3''-trimethoxy-4,4',4''-triacetoxytriphenylcarbinol (7) [1]. The reaction followed a different course when the conditions used were milder, as when a mixture of the hydrochloride of the dye was triturated in a mortar with anhydrous sodium acetate and with a small amount of acetic anhydride. The viscous reaction mass produced at the start thickened gradually and grew lighter in color. After the lapse of some time, the mixture hardened into a yellow clump. It was crushed to a fine powder, washed with water and then with a small quantity of ether, and crystallized from alcohol. This yielded golden-orange crystalline spangles that fused sharply at 129-130°. The yield of the substance was 70% of the theoretical.

The fact that the synthesized substance had a higher color than the original dye and, in contrast to the dye, did not react with a cold solution of sodium bicarbonate was an indication that acetylation had occurred. As we know [2], fuchsone derivatives that contain hydroxy groups dissolve rapidly in solutions of weak alkalis, including sodium bicarbonate, yielding the corresponding brightly colored anions. Rubrocol dissolves, exhibiting a bright violet color. The substance synthesized from rubrocol when the latter was acetylated under the conditions set forth above did not dissolve when placed in a bicarbonate solution. Only after it was heated did it slowly dissolve, as a result of saponification, coloring the solution the typical violet of the rubrocol anion.

The acetyl derivative in question was saponified incomparably faster when it was treated with mineral acids or caustic alkalis. When hydrochloric acid or a 1% solution of sodium hydroxide was added to an alcoholic solution of the substance, the color of the corresponding rubrocol salt soon made its appearance. Colorimetric measurements indicated that when an alcoholic solution of the acetyl derivative in question was heated with 1% sodium hydroxide, it was quantitatively converted into a rubrocol salt.

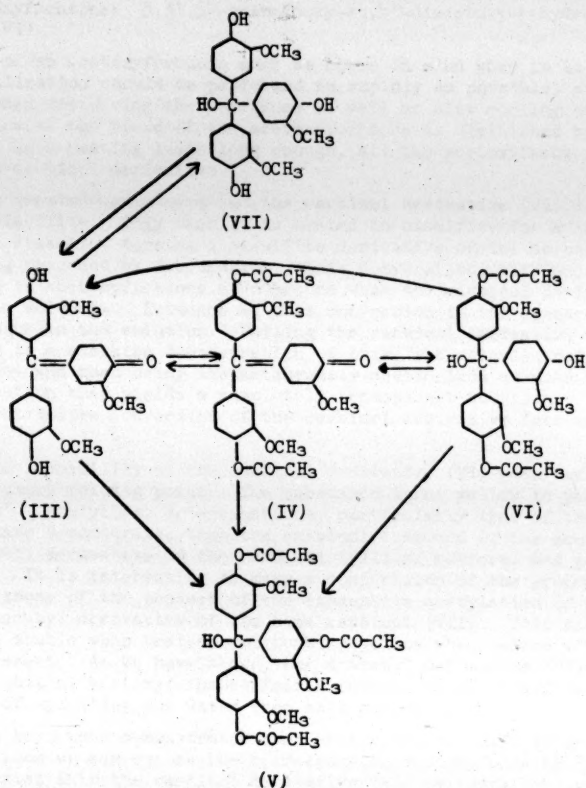
As has been said before [1], the product of the exhaustive acetylation of rubrocol (V) is converted into a salt of the initial dye by saponification. In contrast to this colorless acetyl derivative, however, the colored product of the acetylation of rubrocol described above reacts readily with sodium bisulfite, yielding colorless and transparent solutions of the bisulfite derivative. This is an indisputable sign that the methylenequinone (fuchsone) group is retained in this acetyl derivative.

The resulting bisulfite derivative, like the bisulfite derivative of the unacetylated dye, is decomposed very readily by mineral acids and alkalis. But in the case of the acetyl derivative this is accompanied by saponification of the acetoxy groups. That is why the acetoxy compound cannot be regenerated from its bisulfite derivative, only the original dye being recoverable. Essential differences between the bisulfite derivative of the acetoxyfuchsone and the bisulfite derivative of the unacetylated dye are, on the one hand, the greater stability of the former when reacted with bicarbonate and when stored, and on the other, its higher solubility in water. The bisulfite derivative of rubrocol is only moderately soluble in water, an abundant precipitate settling out when a heated concentrated solution was cooled. The bisulfite derivative of the acetyl derivative is very freely soluble in water and can be isolated by evaporating an alcoholic or aqueous-alcoholic solution.

All these qualitative reactions of the colored product of the acetylation of rubrocol indicate that this compound retained the fuchsone group and that only the hydroxy group of the dye reacts with the acetylating agent during acetylation. This has been confirmed by an elementary analysis and by determination of the number of acetyl groups. The synthesized colored product of the acetylation of rubrocol thus has the structure of 3,3',3"-trimethoxy-4',4"-diacetoxyfuchsone (IV) and is a representative of the acetoxyfuchsones not described up to now.

When this acetoxyfuchsone was heated with acetic anhydride, the colorless product of the exhaustive acetylation of rubrocol (V) described previously [1] was secured. (See next page for scheme).

Like all fuchsone compounds [3], acetoxyfuchsone (IV) adds a molecule of water and is converted into the colorless carbinol derivative (VI). We had previously demonstrated [3] that this hydration of the fuchsones takes place under various conditions, depending upon the presence and number of their hydroxy groups. The hydroxyfuchsone dyes of the aurin series, containing 2 hydroxy groups, rubrocol



among them, are hydrated only in a strongly alkaline medium, giving rise, in the case of rubrocol, for example, to the extremely unstable carbinol derivative (VII), turning into the original dye even when attempts are made to isolate it. Benzaurin and similar hydroxyfuchsone dyes, which contain only one hydroxy group, are converted into carbinol derivatives under milder conditions, when acted upon by more highly diluted alkalis; while the fuchsones and their derivatives that contain no free hydroxy groups are hydrated in a weakly alkaline and even in a neutral medium [4], yielding more stable carbinol derivatives.

The colored acetyl derivative of rubrocol that possesses the acetoxyfuchsone structure (IV) follows the same pattern. Its hydroxy groups are protected by the acetyl radicals, and - like an unsubstituted fuchsone, it is very readily hydrated. We found that this hydration took place even when the acetoxyfuchsone was dissolved in heated aqueous alcohol. As heating was continued, the orange color of the solution gradually turned to light yellow, while the cooled solution did not throw down the acetoxyfuchsone, which, is only very slightly soluble as such in cold alcohol. Only when this solution was diluted with water did a colorless substance settle out - a hydration product, constituting the carbinol deri-

vative of the acetoxyfuchstone: 3,3',3"-trimethoxy-4',4"-diacetoxy-4-hydroxy-triphenylcarbinol (VI).

This property of an acetoxyfuchstone must be borne in mind when it is crystallized. Crystallization should be performed as rapidly as possible, avoiding prolonged heating when dissolving the substance as well as slow cooling of the hot solution. Otherwise the yield of the acetoxyfuchstone is diminished by the ensuing hydration; when heating lasts long enough, all the acetoxyfuchstone can be converted into a carbinol derivative.

In contrast to the acetoxyfuchstone (IV), the carbinol derivative (VI) is insoluble in sodium bisulfite. Only when it is heated in bisulfite for a long time does it slowly dissolve, forming a bisulfite derivative of the acetoxyfuchstone, this being preceded by dehydration. This dehydration, with accompanying conversion into an acetoxyfuchstone also occurs when the carbinol derivative is heated in organic solvents. Evidence of this conversion is the appearance of an orange-yellow color in the solution. Boiling the carbinol derivative with glacial acetic acid is a striking demonstration of this, the solution quickly turning orange-yellow and then being instantaneously decolorized as more bisulfite is added. Dilution then yields a completely transparent solution. This is proof of the quantitative conversion of the carbinol derivative into an acetoxyfuchstone.

Because of this instability of the carbinol derivative (VI) when heated, it does not possess a sharp melting point. The substance turns yellow in part and decomposes at 70-80°. Analytical determinations, particularly that of the number of acetyl groups, have demonstrated that the carbinol compound of the acetoxyfuchstone is a diacetyl derivative of the carbinol (VII) of rubrocol and possesses the structure (VI). It is interesting to make a comparison of the properties of this substance and those of the product of the exhaustive acetylation of rubrocol (V), which is a triacetyl derivative of the same carbinol (VII). This triacetyl derivative is quite stable when heated, not turning yellow when heated with or without solvents present. As we have shown, the diacetyl derivative (VI) is converted into the initial acetoxyfuchstone fairly easily, which is attributable to the feasibility of splitting out water from this compound.

Our researches have thus demonstrated that when rubrocol (III) is acetylated under milder conditions we can secure the corresponding acetoxyfuchstone (IV), which is reversibly converted into the carbinol derivative (VI) by hydration, while more severe conditions yield the product of the exhaustive acetylation, with the triacetyloxycarbinol structure (V). All these substances can be transformed by mutual interactions as shown in the diagram.

It was found that rubrocol could be acetylated to the acetoxyfuchstone (IV) under other conditions as well, especially by dissolving the dye in a mixture of pyridine and acetic anhydride. The color of the solution rapidly faded, though it remained orange even when allowed to stand for a long time. When the solution was diluted with water, a precipitate settled out that hardened into an orange clump. By washing the latter with ether we secured a low yield of the acetoxyfuchstone (IV), all of whose properties were identical with those described earlier. But under these conditions considerable amounts of the carbinol derivative (VI) were formed even during the processes of isolating and purifying the substance. This is probably due to the presence of the pyridine, which promotes the hydration of fuchstone compounds as we know [4].

The dissolution in a mixture of pyridine and acetic anhydride, of other hydroxyfuchstone dyes, such as aurin, benzaurin, and dimethoxybenzaurin, likewise results in the acetylation of nothing but the hydroxy groups, the fuchstone group

not being affected. This is proved by the fact that the crude reaction products are nearly 100% soluble in bisulfite. Our endeavors to isolate these acetoxyfuchsons in an analytically pure state met with failure, however. These substances undergo hydration so readily that this takes place much faster when attempts are made to crystallize them than is the case in the rubrocol acetoxyfuchson. The recovery of the rubrocol acetoxyfuchson in the pure state is also facilitated by the circumstances that it is sparingly soluble in ether and in alcohol; the other acetoxyfuchsons we have synthesized are more soluble, and once dissolved, are quickly converted into the respective carbinol derivatives. Nonetheless, the analytical determination of the acetic acid consumed in acetylation, and of the acetoxy groups in the crude products, sufficed to show that under the specified conditions the reaction principally involved the hydroxy groups, leaving the fuchson group untouched. This is borne out by the fact that fuchsons that contained no hydroxy groups suffered no change when placed in a mixture of acetic anhydride and pyridine. Only when the acetylating mixture was diluted with water were they converted into the corresponding carbinol derivatives, which is a general property of the fuchsons, as has been pointed out previously [4].

EXPERIMENTAL

Synthesis of 3,3',3"-trimethoxy-4,4"-diacetoxyfuchson. a) 22 g of rubrocol hydrochloride and 22 g of anhydrous sodium acetate were placed in a dry mortar and ground to a fine powder, after which the mixture was triturated with 22 g of acetic anhydride. The resulting thick, tacky, dark-brown mass gradually solidified upon standing, its color growing lighter, and turning into a solid yellow clump within 2-3 hours. It was crushed to a powder, washed with water, filtered out, squeezed out well, and dried. Then the substance was placed in 50 ml of ether, agitated, and filtered out. The deposit was added to 200 ml of boiling alcohol, the hot solution being quickly filtered to eliminate any impurities, and the filtrate being immediately chilled with an ice-water mixture while stirred. The acetylation product settled out as golden-orange crystals with a m.p. of 119-120°, the yield being 18.5 g, or some 80% of the theoretical.

b) 9.5 g of the rubrocol base was placed in a mixture of 50 g of pyridine and 10 g of acetic anhydride. The dye dissolved quickly, yielding a transparent orange solution. The latter was poured, with constant stirring, into 500 ml of water. The drops of oil that settled out at first gradually solidified into yellow lumps. The lumps were filtered out, pulverized, washed with water, and dried. The resultant deposit was heated in 50 ml of ether, golden crystals with a m.p. of 115-118° settling out of the ether solution. The yield was 1 g. Some more of the acetoxyfuchson was recovered from the residue that was insoluble in the ether by means of crystallization from alcohol under the conditions specified above.

3,3',3"-trimethoxy-4,4"-diacetoxyfuchson consists of golden-orange crystalline spangles. Its melting point rose to 129-130° after several rapid crystallizations (under the above-mentioned conditions) from alcohol or ether. The substance is insoluble in water, sparingly soluble in ether and cold alcohol, and soluble in hot alcohol, in benzene, and in glacial acetic acid. The solution was decolorized when sodium bisulfite was added to a heated alcoholic or acetic-acid solution, subsequent dilution with water yielding the colorless, transparent solution of the bisulfite derivative. The latter did not crystallize upon cooling, even from concentrated solutions, being recovered only when an aqueous or aqueous-alcoholic solution was evaporated.

The acetoxylfuchsones are rapidly saponified by hydrochloric and sulfuric acids and by alkalis, the corresponding rubrocol salts being formed. The acetoxylfuchsones are unaffected by heating in glacial acetic acid. When it is heated with acetic anhydride, the orange color of the solutions grows paler, dilution with water yielding a colorless precipitate, which had a m.p. of 156-158° after crystallization from alcohol and all of whose properties were identical with those of the product of the exhaustive acetylation of rubrocol - 3,3',3"-trimethoxy-4,4',4"-triacetoxyltriphenylcarbinol [2].

The acetoxylfuchsones are hygroscopic, rapidly gaining weight when exposed to the air, and losing the water of crystallization when dried out at about 100°. When kept in a box in a desiccator it is stable for a considerable period of time. When the acetoxylfuchsones are heated in aqueous alcohol or in aqueous acetic acid, the solution gradually grows paler. Diluting such a solution with water throws down a colorless carbinol derivative - 3,3',3"-4,4',4"-diacetoxyl-4-hydroxy-triphenylcarbinol.

0.1434 g subs.: 0.3536 g CO₂; 0.0691 g H₂O; 0.1310 g subs.: 0.3221 g CO₂; 0.0649 g H₂O. Found %: C 67.25, 67.07; H 5.35, 5.5. C₂₈H₂₄O₈. Calc. %: C 67.24, H 5.12.

A sample of the substance was dissolved in alcohol and saponified with alkali, acetic acid being driven off with steam after sulfuric acid had been added.

0.2148 g subs.: 9.4 ml 0.1 N. NaOH; 0.2304 g subs.: 9.76 ml 0.1 N. NaOH. Found %: CH₃CO groups: 18.8, 18.22. C₂₂H₁₆O₈(CH₃CO)₂. Calc. %: CH₃CO groups 18.54.

Hydration of 3,3',3"-trimethoxy-4,4',4"-diacetoxylfuchsones. 5 g of the acetoxylfuchsones was placed in 200 ml of 50% alcohol, and the resulting mixture was boiled for 4 hours. 1 ml of a sodium bisulfite solution was added to the faintly-yellow resultant solution, which was then diluted with 800 ml of water. The colorless precipitate that settled out collected in clumps that were faintly yellow; they were filtered out, washed with water, and dried. The yield was 5 g. The precipitate secured was purified by redissolving it in 100 ml of 50% alcohol containing 1 ml of bisulfite, filtering, and then adding the filtered solution drop by drop to 500 ml of water that was stirred very vigorously and chilled externally with ice. When the procedure was carried out with care, the reaction product settled out as wholly colorless flocs, which were filtered out, washed with water, and desiccated in a vacuum desiccator with solid potassium hydroxide. The product yield was 4.5 g.

The substance has an unsharp melting point at 70-80°, turning yellow. It is freely soluble in alcohol, ether, benzene, and acetic acid. When the solutions are heated, they turn yellow. The substance does not react with bisulfite, but reacts instantly with it when heated in glacial acetic acid (the solution turning orange-yellow). The substance is saponified very readily by acids and alkalis, yielding salts of rubrocol.

0.2114 g subs.: 8.92 ml 0.1 N. NaOH. Found %: CH₃CO groups: 18.14. C₂₂H₂₀O₇(CH₃CO)₂. Calc. %: CH₃CO groups: 17.85.

SUMMARY

Rubrocol (3,3',3"-trimethoxylaurin) has been used as an example to show that when hydroxylfuchsones dyes are acetylated, the reaction may be confined to the dyes' hydroxy groups if the conditions used are mild enough, their methylenequinone group being preserved. This results in the formation of orange-colored acetoxylfuchsones, hitherto undescribed, which are converted by further acetylation, this

time involving the quinone group — into products of exhaustive acetylation, with a polyacetoxypolyphenylcarbinol structure.

The acetoxypuchsones are readily hydrated, turning into the respective colorless carbinol derivatives; the latter are reconverted into the acetoxypuchsones by heating or by treatment with dehydrating agents.

The acetoxypuchsones react with a bisulfite solution, yielding bisulfite derivatives that are freely soluble in water.

When the acetoxypuchsones are treated with acids or alkalies, they are rapidly saponified, being converted into the corresponding salts of the hydroxypuchsones dyes.

The hydroxypuchsones dyes can also be acetylated to acetoxypuchsones by dissolving the dyes in a mixture of pyridine and acetic anhydride.

LITERATURE CITED

- [1] I. S. Ioffe, J. Gen. Chem., 21, 1316 (1951).¹⁾
- [2] M. Gomberg, J. Am. Chem. Soc., 47, 198 (1925).
- [3] I. S. Ioffe, J. Gen. Chem., 17, 1904 (1951).
- [4] I. S. Ioffe and Z. Ya. Khavin, J. Gen. Chem., 20, 158 (1950).²⁾

Received September 14, 1949.

¹⁾ See Consultants Bureau English translation, p. 1439.

²⁾ See Consultants Bureau English translation, p. 161.

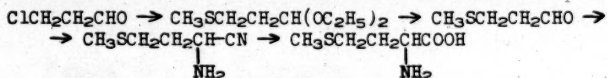
THE ACTION OF AROMATIC DIAZO COMPOUNDS UPON ALKYLACETOXY ESTERS AS A METHOD
OF SYNTHESIZING ARYL HYDRAZONES OF α -KETO ACIDS, α -AMINO ACIDS, AND
INDOLE DERIVATIVES

XII. THE SYNTHESIS OF $\underline{d,l}$ -METHIONINE

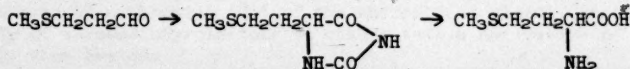
V. V. Feofilaktov and T. N. Ivanova

With the objective of extending the field of applicability of the method developed by one of the present authors for synthesizing the α -amino acids via the aryl hydrazones of α -keto acids, produced in turn from alkyl acetoxy esters [1-5], we have tested the feasibility of synthesizing methionine preparatively in this manner.

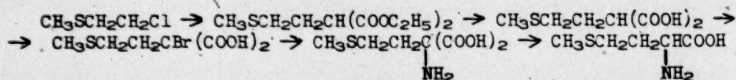
The syntheses of methionine published up to the present time are based upon a cyanhydrin method, a method involving malonic and cyanacetic esters, and a method employing α -aminobutyrolactone. Barger and Coyne [6] effected the first synthesis of methionine in 1928, using the cyanhydrin method and starting with β -chloropropionaldehyde. The methionine yield was 6%, based on the β -methylmercaptopropionaldehyde:



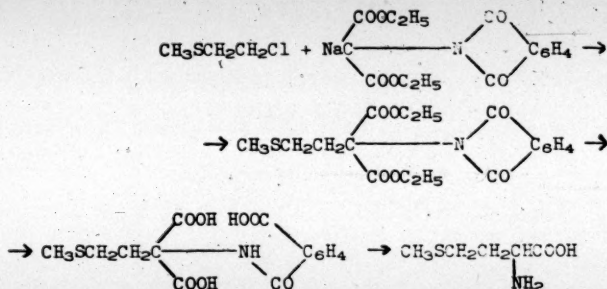
Later, Cath and Graham [7] discovered a much more convenient method of preparing β -methylmercaptopropionaldehyde, improving the yield by directly reacting acrolein with methanethiol in the presence of traces of triethylamine and securing methionine by the cyanhydrin method with a yield of 29%, based on the acrolein. Pierson, Gilla, and Tishler [8] employed the previous authors' method and improved the final stages of the synthesis of methionine by the cyanhydrin method. They converted the β -methylmercaptopropionaldehyde directly into a derivative of hydantoin by a Bucherer reaction (reacting ammonium carbonate and hydrocyanic acid with the aldehyde in alcohol) and transforming the latter derivative into methionine by means of hydrolysis; the yield was 70% of the theoretical, based on the hydantoin derivative:



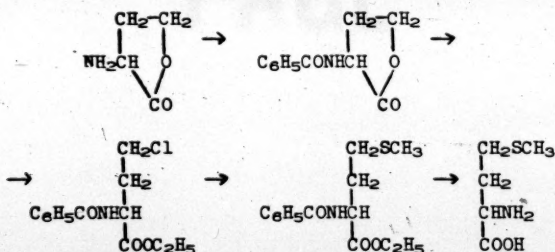
Methionine was synthesized, using malonic ester, in 1930 by Windus and Marvel [9], who started out with β -chloroethyl methyl sulfide and secured a 24% yield of methionine as follows:



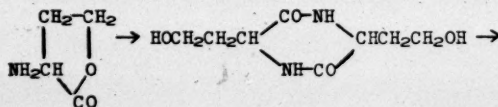
Barger and Weichselbaum [10] improved the methionine yield considerably (54% of the theoretical) by using β -chloroethyl methyl sulfide and phthalimido-malonic ester:

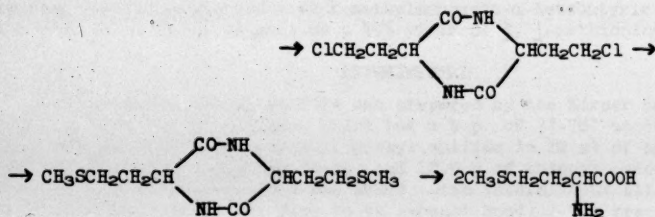


Albertson and Tullar [11] used acetamidocyanacetic ester in the synthesis of methionine, while Goldsmith and Tishler [12] used acetamidomalonic ester. α -Aminobutyrolactone has been extensively used in recent years in the synthesis of methionine. The first synthesis of this kind was effected in 1936 by Hill and Robson [13], the authors synthesizing the required α -aminobutyrolactone by a rather roundabout process:

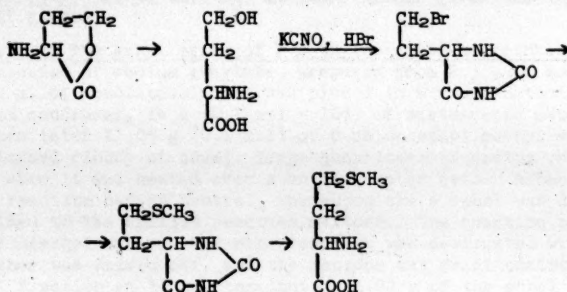


The research of Knunyants, Chelintsev, and Osetrova [14] and of Feofilaktov and Onishchenko [15] has made α -aminobutyrolactone a readily available compound, and in 1942 Snyder, Andreen, and their co-workers [16] effected a fully satisfactory synthesis of methionine (85% of the theoretical yield), employing the well-known ability of α -aminobutyrolactone to change into a derivative of diketopiperazine readily when heated:

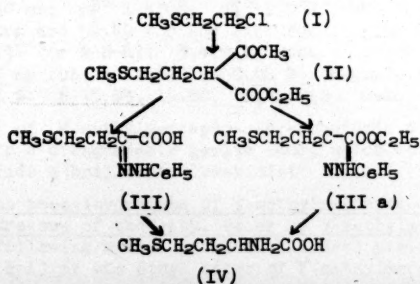




In 1945, Livak, Britton and others [17] synthesized methionine from α -amino-butyrolactone via hydantoin. The yield was 95% of the theoretical, based on the hydantoin derivative:



We have synthesized methionine as follows:



The initial substances we used were acetoacetic ester and β -chloroethyl methyl sulfide. β -Chloroethyl methyl sulfide (I) reacts readily with sodium acetoacetate to give a 54% yield of the ethyl ester of γ -methylmercapto- α -aceto-butyric acid (II). The azo coupling of this ester with phenyldiazonium chloride yielded the phenylhydrazone of γ -methylmercapto- α -ketobutyric acid (III), the yield being 73% of the theoretical, while several modifications in the azo coupling procedure yielded the phenylhydrazone of the ethyl ester of γ -methylmercapto- α -ketobutyric acid (III a) with a yield that was 71% of the theoretical. To the best of our knowledge these compounds have not been described in the literature.

Reducing the phenylhydrazone of γ -methylmercapto- α -ketobutyric acid (III) with zinc dust in acetic acid gave us a 49% yield of d, l-methionine (IV).

EXPERIMENTAL

β -Chloroethyl methyl sulfide was prepared by the Kirner method [18]. from β -hydroxyethyl methyl sulfide, which had a b.p. of 77-78° at 30 mm; n_D^{20} 1.4851 9.2 g (0.1 mol) of β -hydroxyethyl methyl sulfide in 12 ml of anhydrous chloroform was placed in a Claisen flask, and 12.5 g of thionyl chloride dissolved in 12 ml of anhydrous chloroform was added, with intermittent stirring, in the course of 20-30 minutes (this was done in an exhaust hood). The reaction mixture was allowed to stand for at least one hour at room temperature, after which the chloroform was driven off over a water bath. The residue was fractionated in vacuum twice, the β -chloroethyl methyl sulfide secured (8.62 g, 78% of the theoretical yield, based on the β -hydroxyethyl methyl sulfide used) having the following constants: b.p. 55-57° at 30 mm; n_D^{20} 1.4908. Kirner gives the b.p. as 55-56° at 30 mm and n_D^{20} 1.4902.

Synthesis of the ethyl ester of γ -methylmercapto- α -acetobutyric acid (II). A chilled solution of sodium ethylate, prepared from 2.3 g of sodium (0.1 gram-atom) and 40 ml of absolute alcohol was placed in a round-bottomed flask fitted with a reflux condenser, 14 g (0.1 mol + 10%) of acetoacetic ester was poured in, and 20 minutes later 11.05 g (0.1 mol) of β -chloroethyl methyl sulfide was added. The liquid turned cloudy at once; large quantities of sodium chloride were thrown down when it was heated over a boiling water bath. After three hours of heating the reaction became neutral, whereupon the alcohol was driven off, and water was added to the chilled reaction mixture. The reaction product was extracted with diethyl ether. The ether extract was desiccated with sodium sulfate, the ether was driven off, and the residue was fractionated twice in vacuum. The 164-166° fraction at 30 mm constituted 11.02 g of the ethyl ester of γ -methylmercapto- α -acetobutyric acid (54% of the theoretical, based on the β -chloroethyl methyl sulfide) and had the following constants:

b.p. 164-166°/30 mm; n_D^{20} 1.4768; d_4^{20} 1.0697; M_R 53.85; Calc. 53.45 for the keto form and 54.49 for the enol form. (The atomic refraction of sulfur is 7.97 for R-S-R). 3.470 mg subs.: 1.724 ml 0.02 N $Na_2S_2O_3$. 3.837 mg subs.: 1.892 ml 0.02 N. $Na_2S_2O_3$ (N. E. Gelman's method). Found %: S 15.93, 15.80. $C_8H_{16}O_3S$. Calc. %: S 15.68.

The ethyl ester of γ -methylmercapto- α -acetobutyric acid is a mobile colorless liquid with a disagreeable garlic odor, which colors an aqueous solution of ferric chloride a brilliant blue-violet.

Synthesis of the phenylhydrazone of γ -methylmercapto- α -ketobutyric acid (III) and of the phenylhydrazone of the ethyl ester of γ -methylmercapto- α -ketobutyric acid (III a). The following method provided the best yields of the phenylhydrazone. 4.08 g (0.02 mol) of the ethyl ester of γ -methylmercapto- α -acetobutyric acid was added to sodium ethylate (0.46 g of sodium (0.02 gram-atom) in 24 ml of absolute alcohol) cooled to room temperature. The resulting sodium derivative was kept at room temperature for 30 minutes (Solution A). The solution of phenyldiazonium was prepared in the usual manner from 2.3 g (0.02 mol) of aniline hydrochloride, 11 ml of water, 2.2 ml of hydrochloric acid (d 1.19), and 1.4 g (0.02 mol) of sodium nitrite dissolved in 5 ml of water (solution B). 4.4 g of crystalline sodium acetate dissolved in 10 ml of water (Solution C) was placed in a porcelain beaker fitted with a mechanical stirrer and chilled on the outside with ice. Solution C was stirred vigorously while the chilled Solutions A and B were added drop by drop. The mixture at once turned brown-red, after which a red-brown

oil settled out as drops on the walls of the beaker and the blades of the stirrer. Stirring was continued for 4 hours, although the reaction for free diazonium was negative earlier. The reaction product (the oil) was extracted with diethyl ether. After the ether had been driven off, we were unable to crystallize the residual oil, and we then saponified it by heating it with an aqueous-alcoholic solution of potassium hydroxide (1.5 g of KOH in 30 ml of alcohol and 3 ml of water) over a water bath with a reflux condenser for 2 hours. Then the alcohol was driven off, and water was added a little at a time to the distilling flask; the neutral tarry products were extracted with diethyl ether, and the alkaline aqueous solution was ice-chilled and then acidified with hydrochloric acid. The phenylhydrazone of γ -methylmercapto- α -ketobutyric acid was recovered as fluffy yellow flocs. The product weighed 3.47 g (73% of the theoretical yield) after being filtered out and dried in a desiccator, fused at about 85°, and exhibited a distinct Bulow reaction (reddish-violet color with concentrated sulfuric acid and potassium dichromate). The substance is freely soluble in alcohol, ether, acetone, and chloroform, and when heated in acetic acid and benzene; it is insoluble in petroleum ether. Triple recrystallization from an alcohol-water mixture yielded the substance as extremely light light-orange leaflets with a m.p. of 96-97°.

3.845 mg subs.: 0.395 ml N₂ (21°, 754 mm). 3.867 mg subs.: 0.390 ml N₂ (20°, 753 mm). Found %: N 11.84, 11.64. C₁₁H₁₄O₂N₂S. Calc. %: N 11.76.

An alcoholic solution of the phenylhydrazone was titrated with aqueous sodium hydroxide (against phenolphthalein). 0.1080 g subs.: 4.65 ml. 0.1 N NaOH. Found equiv.: 233.5. C₁₁H₁₄O₂N₂S. Calc. equiv.: 238 (monobasic acid).

We found that when a small amount of an aqueous-alcoholic solution of potassium hydroxide was reacted with the crude oily product of the coupling reaction, the oil dissolved, an orange-colored crystalline precipitate - the phenylhydrazone of the ethyl ester of γ -methylmercapto- α -ketobutyric acid - settling out when the solution was poured into water containing ice. In one of our tests this yielded 71% of the theoretical product, based on the phenylhydrazone of the ethyl ester of γ -methylmercapto- α -ketobutyric acid. The substance displayed a positive Bulow reaction, and was freely soluble in alcohol, ether, and acetone, less so in acetic acid and benzene, and insoluble in petroleum ether. Triple recrystallization of the product from a mixture of alcohol and water yielded fine, elongated, yellow needles with a m.p. of 91-92°.

4.695 mg subs.: 0.449 ml N₂ (25°, 744 mm). 4.380 mg subs.: 0.412 ml N₂ (24°, 742 mm). Found %: N 10.72, 10.56. C₁₃H₁₈O₂N₂S. Calc. %: N 10.52.

The structure of the resultant product was established as that of the phenylhydrazone of the ethyl ester of γ -methylmercapto- α -ketobutyric acid (IIa) by saponifying it by heating it over a water bath with a 10% alcoholic solution of potassium hydroxide, acidulation yielding the phenylhydrazone of γ -methylmercapto- α -ketobutyric acid, which fused at 97°. A fusion sample mixed with a preparation synthesized by the direct saponification of the oily product of the coupling reaction exhibited no depression.

Reduction of the phenylhydrazone of γ -methylmercapto- α -ketobutyric acid (III) to d, l-methionine (IV). 2.38 g (0.01 mol) of the phenylhydrazone of γ -methylmercapto- α -ketobutyric acid (not recrystallized) and 24 ml of glacial acetic acid were placed in a round-bottomed flask fitted with a reflux condenser. All the phenylhydrazone dissolved when the flask was heated over a water bath. Zinc dust was added to the flask a little at a time as dissolution progressed. The color of the reaction liquid vanished after one hour had elapsed, a total of 4 g of zinc dust having been added. The 24 ml of water was added in two batches of 12

ml each spaced 30 minutes apart, and heating was continued for another hour. When reduction was complete (as was indicated by the negative Bulow reaction), the flask contents were treated with diethyl ether, and the zinc was eliminated by passing hydrogen sulfide through the flask. The filtrate and the zinc-sulfate wash water were combined and evaporated to dryness at 60-70° in vacuum. The dry residue was dissolved in a small quantity of hot water, and three times the volume of absolute alcohol was added to the hot-filtered solution. The methionine settled out as characteristic colorless elongated hexagonal tablets, with a high mother-of-pearl luster. Some more of the amino acid was recovered from the mother liquor, a total of 0.73 g of methionine being secured (49% of the theoretical yield). The product had a m.p. of 269-270° (with decomposition in a sealed capillary) after it had been recrystallized from hot water by adding absolute alcohol.

5.230 mg subs.: 0.444 ml N₂ (20°, 753 mm). 4.200 mg subs.: 0.350 ml N₂ (20°, 754 mm). 3.205 mg subs.: 2.152 ml 0.02 N Na₂S₂O₃. 3.041 mg subs.: 2.032 ml 0.02 N Na₂S₂O₃ (Gelman's method). Found %: N 9.80, 9.63; S 21.52, 21.42. C₅H₁₁O₂NS. Calc. %: N 9.41; S 21.47.

Odaki [19] gives the m.p. of methionine as 265° (with decomp.), Barger and Coyne [6] giving the m.p. as 281° (with decomp.), Winduus and Marvel [9] giving 272° (with decomp.), and Livak, Britten, and their co-workers [17] 269-270° (with decomp.).

SUMMARY

The V. V. Feofilaktov method - synthesizing the α -amino acids from alkyl-acetoxy esters via the aryl hydrazones of α -keto acids is applicable fairly universally, making it possible to synthesize d,l-methionine under comparatively simple conditions.

The initial substance used in synthesizing d,l-methionine was the ethyl ester of γ -methylmercapto- α -acetoxybutyric acid, secured in a 54% yield from acetoacetic ester and β -chloroethyl methyl sulfide, which was, in turn, prepared from β -hydroxyethyl methyl sulfide.

The azo coupling of the ethyl ester of γ -methylmercapto- α -acetobutyric acid with phenyldiazonium yielded the phenylhydrazone of the ethyl ester of γ -methylmercapto- α -ketobutyric acid (71% yield) and the phenylhydrazone of γ -methylmercapto- α -ketobutyric acid (73% yield).

A yield of 49% of d,l-methionine was secured by reducing the phenylhydrazone of γ -methylmercapto- α -ketobutyric acid.

LITERATURE CITED

- [1] V. Feofilaktov, J. Gen. Chem., 10, 247 (1940).
- [2] V. Feofilaktov and E. Vinogradov, J. Gen. Chem. 10, 254 (1940).
- [3] V. Feofilaktov and V. Zaitseva, J. Gen. Chem., 10, 258 (1940); Ibid., J. Gen. Chem., 10, 1391 (1940); V. Feofilaktov and F. Blanko, J. Gen. Chem., 11, 859 (1941); V. Feofilaktov and V. Zaitseva, J. Gen. Chem., 13, 358 (1943).
- [4] V. Feofilaktov, V. Zaitseva, and K. Sorotkina, J. Gen. Chem., 13, 363 (1943).
- [5] V. Feofilaktov and A. Ivanov, J. Gen. Chem., 13, 457 (1943).
- [6] G. Barger, F. Coyne, Bioch. J., 22, 1417 (1928).
- [7] J. Cath, A. Cook, A. Graham, L. Heilbron, Nature, 159, 578 (1947).
- [8] E. Pierson, M. Gilla, and M. Tishler, J. Am. Chem. Soc., 70, 1450 (1947).
- [9] W. Winduus, C. Marvel, J. Am. Chem. Soc., 52, 2575 (1930).
- [10] G. Barger, T. Weichselbaum, Bioch. J., 25, 997 (1931).
- [11] N. Albertson, B. Tullar, J. Am. Chem. Soc., 67, 502 (1945).

- [12] D. Goldsmith, M. Tishler, J. Am. Chem. Soc., 68, 144 (1946).
[13] E. Hill, W. Robson, Biochem. J., 30, 248 (1936).
[14] I. Knunyants, G. Chelintsev, and E. Osetrova, Dokl. USSR Acad. Sci., 1, 912 (1943).
[15] V. Feofilaktov and A. S. Onishenko, J. Gen. Chem. 9, 304 (1939).
[16] H. Snyder, G. Andreen, G. Cannon, C. Peters, J. Am. Chem. Soc., 64, 2082 (1942).
[17] J. Livak, E. Britton, J. Vander-Weele, M. Murray, J. Am. Chem. Soc., 67, 2218 (1945).
[18] W. Kirner, J. Am. Chem. Soc., 50, 2446 (1928).
[19] S. Odaki, BiochemZ., 161, 446 (1925).

Chair of Organic Chemistry,
The K. A. Timiryazev Agricultural
Academy, Moscow,
Awarded the Order of Lenin

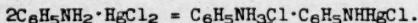
Received December 25, 1949.

THE ACTION OF ELEMENTS OF THE OXYGEN-SULFUR-SELENIUM GROUP ON PRIMARY AROMATIC AND HETEROCYCLIC AMINES

P. S. Pishchimuka

Elementary sulfur can combine with hydrogen directly, forming hydrogen sulfide and generating heat. This reaction occurs at an appreciable velocity, however, only when the reagents are heated to a fairly high temperature. Organic hydrides likewise give off H_2S when heated with sulfur to $250-300^\circ$. H_2S is also generated when aniline is boiled for a long time with sulfur. Although the energy of the bond between the hydrogen and the nitrogen in the amino group is lower than that of the bond between hydrogen and carbon in the aromatic ring, the reaction entailing the formation of H_2S always involves the hydrogen atoms attached to carbon in aniline (and other aromatic amines), the hydrogen atoms in the amino groups remaining unaffected. The action of sulfur upon aromatic amines results in the formation of nothing but thiodiamines, such as $(NH_2C_6H_4)_2S$ from aniline.

This phenomenon, which is incomprehensible at first glance, can be explained quite readily. If the H_2S were produced from the hydrogen atoms of the amino groups, an aromatic amine would yield hydrazo or azo compounds; we know that the latter are very easily reduced to the initial amine by hydrogen sulfide. It must be assumed that the H_2S is principally (and possibly exclusively) formed from the hydrogen atoms in the amino groups (and, it may be, at even lower temperatures), but this formation is masked by the high-velocity reverse reduction reactions; only when the temperature has been raised high enough does the hydrogen begin to split out of the carbon ring and form thioamines that cannot be reduced by hydrogen sulfide. In fact, if we employ substances that can bind H_2S directly as soon as it is formed, the reaction between the sulfur and the amine occurs readily, even in the cold, and all the H_2S is evolved from the hydrogen atoms of the amino groups, the hydrogen atoms in the ring remaining untouched. This splitting out of hydrogen converts aromatic amines into azo and hydrazo compounds. Under the prevailing reaction conditions the latter (diphenylene, benzidine, and semidine) undergo the intramolecular rearrangements that are characteristic of these compounds, the further dehydrogenation by sulfur yielding azines and thiazine dyes as secondary products. Of the many products that can bind the H_2S evolved in this reaction without retarding the reaction itself, only the nitrogenous compounds of mercury proved to be suitable, provided, however, that at least one of the mercury's valence bonds be attached to the nitrogen atom. This condition is satisfied by the mercury derivatives of acid amides and imides and by amines of mercury salts. Mercury salts can also bind H_2S in this reaction, but only when they constitute double compounds with the reacting amine. Mercuric chloride and aniline form the compound $2C_6H_5NH_2 \cdot HgCl_2$, for example. It may be readily shown that the structure of this compound is such that one of the mercury's valence bonds is attached directly to the nitrogen atom:



If the mercury salt cannot form a double compound with the amine, it is totally useless for the reaction in question, the only reaction products secured then being thioamines. When a passive salt of this sort is converted into its amine, the latter gives rise to the same products as the mercury derivatives of amides and imides (i.e., azines and dyes) in the reaction of the amine with sulfur.

We have been able to prove that when a mercury-nitrogen compound possessing two bonds between the mercury and the nitrogen (mercury-substituted amides and imides) is involved in the reaction of sulfur with an aromatic amine, the bulk of the reaction product consists of azo compounds, the formation of other products being secondary. If the mercury-nitrogen compound contains only one nitrogen atom attached to the mercury, the sole products formed are azines and dyes. The reaction is smooth in the former case (rapid and with a high yield of azo compounds), but is much slower in the latter case, requiring prolonged heating (as much as several days) at 100-150°.

We effected the reaction of an amine with sulfur and a mercury-nitrogen compound in a neutral liquid medium (hydrocarbons and halogen derivatives) by digestion in the cold or by boiling (for the retarded reactions). It should be noted that the mercury-nitrogen compounds employed in this reaction are wholly insoluble in the specified liquid media.

The next, heavier, analog of sulfur in the periodic system - selenium - proved to be completely passive with aromatic amines, as might have been predicted. This has been confirmed experimentally by Cornelius [1], who showed that amines do not react with selenium in the cold or when heated, not even in sealed tubes or when catalysts are employed. It was found however, that even selenium converts aromatic amines into azo compounds, azines, and dyes - derivatives of selenium azines - very easily when the specified mercury compounds are used. Hence, here too, the reaction involves the splitting out of hydrogen atoms from the amino groups, as in the case of sulfur. It should be stressed, moreover, that the reaction with selenium is much easier than with sulfur, high product yields being attained. The yields of azo compounds given in the table were obtained in reactions with Se.

I. Aromatic and heterocyclic primary amines. The results of experiments carried out with 26 aromatic and heterocyclic amines served as the basis for our conclusion that primary aromatic and heterocyclic amines are converted into azo compounds, azines, and dyes when reacted with S or Se in the presence of mercury-nitrogen compounds (mercury substituted amides and imides, mercury salts, and amines of mercury salts). These amines are listed in the following table. (see next page).

An apparent exception to this rule is the inability of the ortho nitroamines (o-nitroaniline, o-nitrotoluidine, 2,4,6-nitrochloronitroaniline) to react with either S or Se. Under the prevailing reaction conditions the amino groups are not present in these substances, owing to the presence of a hydrogen bond between the nitro and amino groups. These so-called nitroamines cannot, therefore, be classed as aromatic compounds or as primary amines.

The composition and structure of the amines to be dehydrogenated affect the nature and yield of the reaction products very substantially. Let us cite the following as examples of this. In the presence of mercury acetamide selenium yields as much as 72% of azobenzene from aniline, while sulfur barely yields 3%. This difference between the action of sulfur and selenium disappears almost completely in the reaction with p-dimethylaniline or with the naphthylamines. The ethyl ester of p-aminobenzoic acid yields 85% of an azo compound, while p-amino-

No.	Amine	% yield of azo compound	% yield of dye	No.	Amine	% yield of azo compound	% yield of dye
1	Aniline	71.4	8.3	14	p-Aminophenol....	-	Great
2	m-Nitroaniline.	62.3	Slight	15	Methyl anthra- nilate	-	-
3	p-Nitroaniline.	70.1	Slight	16	Nitroaminophen- ylsulfide-4,4'..	-	-
4	p-Anisidine....	62.3	23.0	17	Diaminodiphenyl sulfide-4,4'....	-	-
5	o-Toluidine....	36.1	29.9	18	Naphthylamine (α)	-	Great
6	m-Toluidine....	60.2	28.1	19	Naphthylamine (β)	-	Great
7	p-Toluidine....	73.3	10.2	20	Sulfanilamide....	-	34% naphth- azine
8	m-Xylidine.....	60.2	Slight	21-23	Phenylenediamines (ortho, meta, and para).....	-	Great
9	Ethyl p-amino- benzoate.....	84.8	5.1	24	Benzidine.....	-	Great
10	p-Chloraniline.	82.3	12.5	25	Aminopyridine (α)	-	-
11	p-Aminoazoben- zene.....	41.5	-	26	Aminoquinoline (β)	70	-
12	o-Toluenazo- toluidine....	78.4	13.9				
13	p-Aminodimeth- ylaniline.....	50.0	Great				

phenol yields none at all under the same reaction conditions. It may be regarded as definitely proved that the ortho isomers produce the lowest yields of azo compounds, and the para isomers the highest.

Thus, the reaction of primary aromatic (and heterocyclic) amines with S and Se is as characteristic of these compounds as their diazotization.

II. Mercury-nitrogen compounds. The author of this report has prepared about 40 different mercury derivatives of acid amines, imides, mercury salts, and the latter's amines. All of them proved to be active in the reaction of aniline (and other primary aromatic and heterocyclic amines) with S (and Se). They were:

Mercury salts: 1-2) mercuric and mercurous chlorides; 3-4) mercurous and mercuric nitrates; 5) mercurous sulfate; 6) mercuric acetate; 7) mercuric phthalate; 8) mercuric urate; 9) mercuric theobromate; 10) mercuric diethyl-barbiturate.

Amines of mercury salts of the following acids:¹ 11) succinic; 12) benzoic; 13) salicylic.

Mercury substitution derivatives of the following amides and imides: 14) acetamide; 15) propionamide; 16) benzamide; 17) phthalamide; 18) phthalimide; 19) succinamide; 20) succinimide; 21) carbamide; 22) biuret; 23) cyanamide; 24) guanidine; 25) cyanoguanidine; 26-27) benzenesulfamide (2 preparations); 28-29) toluenesulfamide (2 preparations); 30-31) sulfanilamide (2 preparations); 32) saccharin; 3) acetylsulfanilamide; 34) sulfazole; 35) sulfinide; 36) pyridylnitramide; 37) mercury aniline; 38) white precipitate.

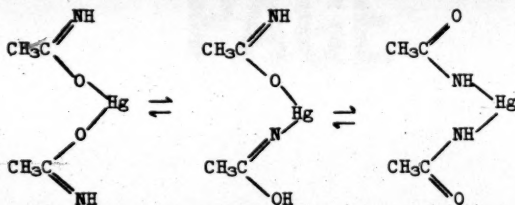
Except for the mercury derivatives of acetamide, propionamide, benzamide, and succinimide, none of the mercury substitution derivatives of the amides or

1) The salts of these acids do not form double compounds with aniline, so that the latter proved to be completely passive with S and Se, no reaction occurring.

imides is soluble in water or in alcohol. The best method of preparing them is to react a solution of mercuryacetamide (readily available) with aqueous or alcoholic solutions of the amides or imides. This yields satisfactorily pure mercury substitution derivatives.

It was asserted above that when S or Se is reacted with primary aromatic (or heterocyclic) amines in the presence of mercury-nitrogen compounds that are known to contain a mercury atom linked to two nitrogen atoms (mercury-substituted amides and imides), symmetrical azo compounds are the principal products of the reaction. When the mercury-nitrogen compounds employed have the mercury linked to a single nitrogen atom (salts, amines), no azo compounds are formed, azines and dyes being synthesized. However, even in the first case the formation of the azo compounds is accompanied by the production of more or less of the dyes. The fact that the dyes always accompany the azo compounds (which constitute the bulk of the reaction product) may be attributable to the presence of tautomeric mercury substitution derivatives of the amides and imides.

We may conclude from the extensive literature on alkyl-substituted amides and imides [2-11] that the amides and imides that are alkyl-substituted at the oxygen atom are chiefly or exclusively formed from amides (or imides) at low temperatures, while those that are substituted at the nitrogen atom are formed at high temperatures. It is therefore obvious that the imino acid form is stable in the cold, being converted into a true amide when the temperature is raised. The same must be true of metallic derivatives of acid amides (and imides), but the transformation of a salt of an imino acid into the form of a metallic derivative of a true amide must involve the formation of intermediate products, which will lie sort of halfway between the salt and the metallic substitution derivative of the amide. In the case of mercury acetamide, this may be depicted as follows:

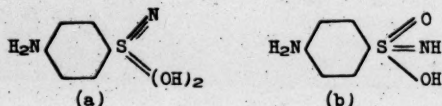


Hg - salt of an imino acid. Intermediate product. Substituted amide.

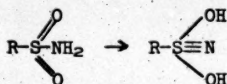
The salt is passive, while dehydrogenation of the intermediate product containing mercury linked to nitrogen and oxygen yields azines and dyes, and that of the amide with mercury attached to the nitrogen and azo compound. A transformation of this sort is conceivable for any metallic substitution derivative of an amide or imide.

Acetamide, benzamide, succinimide, and phthalimide are amido derivatives of weak acids, so that their corresponding metallic substitution derivatives will consist of tautomeric mixtures of all the isomers, even at low temperatures, and the dehydrogenation reaction can occur without the application of heat. Indeed, when the foregoing mercury-substituted amides and imides are used, aniline (like many other aromatic primary amines) yields all three types of reaction product: azo compounds, azines, and dyes even at room temperature (and more quickly when heated). The amides and imides of strong acids, such as sulfanilamide and saccharin, behave otherwise. It is unlikely that the generally accepted amide and

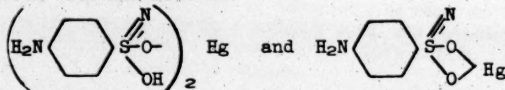
imide forms apply to these compounds. The streptocide, for example, is neutralized by alkaline bicarbonates as well as by alkalis, yielding stable salts. There is no doubt that it is not the amide as such but its isomers: the dibasic sulfanitrido acid (a) and the monobasic sulfanilimino acid (b), that take part in the neutralization process:



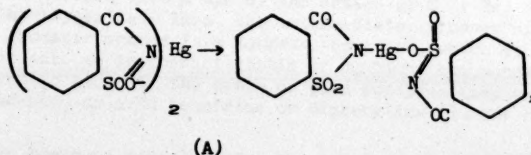
Here we encounter a paradoxical phenomenon. The amino group converts a monobasic sulfonic acid into a dibasic one when it enters the sulfo group:



The author of this report has prepared the mercury salts of sulfanilnitrido acid, both acid and neutral:



The foregoing applies with even greater force to saccharin. The generally accepted structure of the latter as an imide of ortho sulfobenzoic acid is wholly unsuitable. Saccharin is a very strong acid, yielding stable salts with almost all cations. Its dissociation constant is higher than that of acetic acid. Its mercury salt is readily produced by a double decomposition reaction with mercury acetamide. Thus mercurysaccharin is the salt of the isomeric imide of sulfonitrido benzoic acid (A). These mercury salts of the streptocide and of saccharin (like those of other sulfamides) are gradually converted by heating to at least 150° into amides (or imides) that are partially substituted at the nitrogen atom, and only at this temperature do they cause the transformation of aniline into a dye by sulfur or selenium dehydrogenation; no azo compounds are formed. Hence, at 150° the mercury salt, say of saccharin, is isomerized to a mercury imide that is partially substituted at the nitrogen atom:



i.e., into a form that can convert an amine into a dye (presence of the N-Hg-O group).

Depending upon the acids whose derivatives they are, all other mercury amides and imides occupy positions that lie between these two extreme examples: many mercury amide forms existing in the case of mercury acetamide and their almost complete absence in the mercury derivative of saccharin.

Thus there can be no doubt about the relationship between the structure of the mercury derivative and the composition of the dehydrogenation products of aromatic amines.

The conversion of mercury salts of imino acids into substitution derivatives of amides occurs at high temperature, as stated above. The inverse transition of the mercury amide substitution derivative into the form of a mercury salt of an imino acid takes place when the preparation is kept for a long time. Thus, the highly active mercury acetamide proved to be wholly useless for dehydrogenation in the cold after the lapse of 12-15 years. Heating restored its original activity. This is an instance of reversible isomerization by heat, and indicates the tautomerism of mercury amides and imides.

The structure of mercury-nitrogen compounds apparently also depends upon the medium in which they are placed, say the solvent if the substance is in solution. It was established long ago that hydrogen sulfide does not throw down mercuric sulfide from an aqueous solution of mercury acetamide, though HgS is readily formed in an alcoholic solution. It is natural to suppose that the preparation dissolved in water is the mercury salt $\text{Hg}(\text{OCNHCH}_3)_2$, while the one dissolved in alcohol is the substituted amide $\text{Hg}(\text{NHCOCH}_3)_2$. Inasmuch as we know from the foregoing that in an aqueous solution the mercury in mercury acetamide is linked to oxygen, and in an alcoholic solution to nitrogen, we may readily infer that mercury will be split out by hydrogen sulfide more easily when it is linked to the nitrogen in a mercury amide compound, while this action will be harder and, hence, slower, when it is linked to oxygen.

We may now attempt, on the basis of what has been set forth above, to establish the reason for the relationship between the structure of the mercury-nitrogen compounds used in dehydrogenating aromatic amines with sulfur or selenium and the composition of the resulting dehydrogenation products.

III. The mechanism involved in the conversion of amines into azo compounds, azines, and dyes. There can be no doubt about the mechanism involved in the formation of azo compounds by the action of S or Se upon primary aromatic (or heterocyclic) amines. The azo compounds are the products of the junction of two aryl-nitrogen radicals. The structure of the dyes may be determined from the structure of the intermediate reaction products and is confirmed by their identity with dyes produced synthetically.

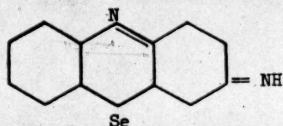
The author of this report has succeeded in reacting α -naphthylamine with S (a less active agent than Se) at low temperature ($4-5^\circ$) and isolating from the reaction products a crystalline substance whose composition and properties (oxidizability to a dye, conversion into a dye by the action of S or Se) indicated it was secondary aminodisnaphthylamine. Thus, the intermediate product of the action of S (Se) on primary aromatic amines is a hydrazo compound, which is isomerized under the reaction conditions, as is characteristic of hydrazo compounds, into a secondary amine with an amino group in the ortho or para position (and ortho or para semidine rearrangement), or into benzidine or diphenylene (in the case of hydrazobenzene) ¹⁾.

If the hydrazo compound formed during the first phase of the reaction undergoes a benzidine (or diphenylene) rearrangement, the resulting diamine reacts further with the S (or Se), repeating this reaction and yielding a group of dyes that may be called benzidine dyes (or diphenylene dyes, respectively).

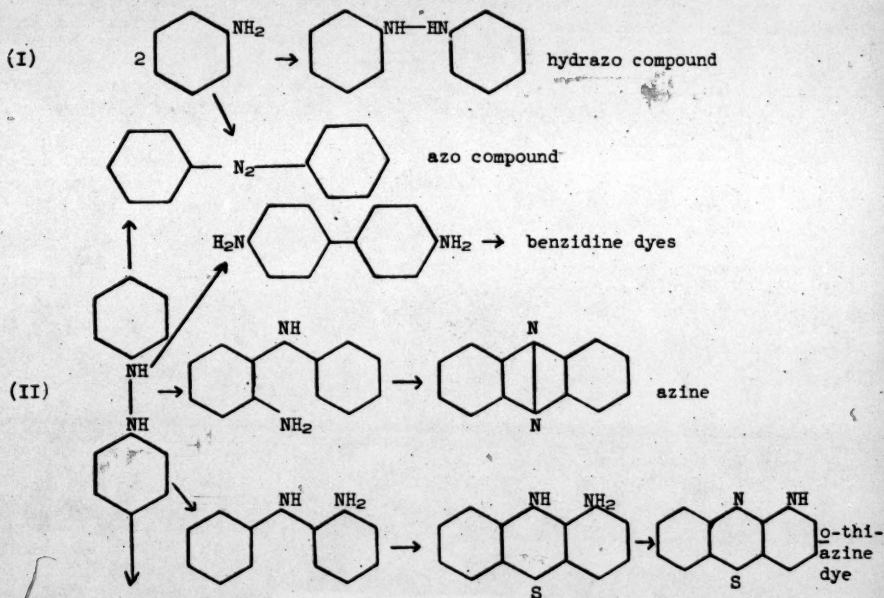
There are two possible cases of an ortho semidine rearrangement. If the S (or the Se) detaches hydrogen atoms from the carbon atoms and from the amino group

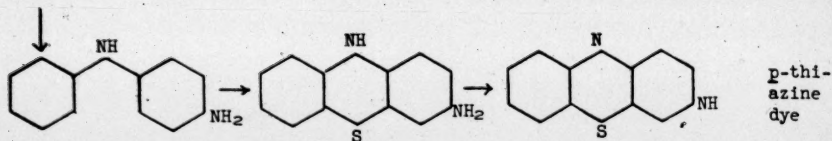
¹⁾ Similar substances are formed, of course, from the other aromatic amines.

3



The considerations set forth above indicate that the following outline of the action of S (or Se) upon primary aromatic (or heterocyclic) amines is satisfactorily established.



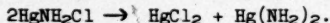


The first product of dehydrogenation, which is formed from every amine, is a hydrazo compound (hydrazobenzene)¹. But this reaction can take place only in the presence of another, parallel reaction, involving the binding of the hydrogen sulfide evolved by a mercury-nitrogen compound. It may also be supposed that the formation of HgS is the source of the energy required for the dehydrogenation reaction. If the H_2S (or H_2Se) is carried away from the field of the reaction fast enough, which requires an adequate quantity of the mercury amide form (N-Hg-N), as is apparent from the foregoing, the subsequent dehydrogenation of the hydrazo compound results in the formation of an azo compound; whereas, if the binding of the H_2S (or H_2Se) meets with difficulty, owing to the absence of the above-mentioned form, dehydrogenation is slowed down, and the hydrazo compound may undergo a series of rearrangements, such as a benzidine rearrangement and ortho and para semidine rearrangements, so that further dehydrogenation results in the formation of the substances depicted in the above diagram: benzidine dyes, ortho and para semidine dyes, and azines.

Hence, the faster the mercury salt of an imino acid and a mixed amido-mercury salt are isomerized into a completely substituted mercury amide, the higher will be the yield of the azo compound, while slowing down of this process results in an increase of azines and dyes among the reaction products at the expense of the azo compound, and the total absence of a mercury-nitrogen compound having a N-Hg-N group makes the formation of any azo compound impossible (mercury salts and amines of mercury salts).

Thus, we see the reason for the relationship between the amount and nature of the products formed in the dehydrogenation of aromatic amines and the presence as well as the relative amount, of the mercury-nitrogen forms present in the tautomeric mixture.

When the infusible precipitate is heated for a long time, it yields a slight amount (up to 3%) of azobenzene from aniline, in addition to the dyes. No isomerization takes place here, of course. The formation of the azo compound may be attributed to the dissociation of the precipitate by heating into a mixture of mercuric chloride and mercury amide:



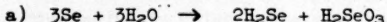
As a rule mercuric chloride forms dyes from aniline, while mercury amide forms azobenzene.

IV. Selenium. Like sulfur, elementary selenium has many allotropic modifications. Some of them display much higher activity in chemical reactions than the analog of selenium consisting of lighter atoms - sulfur. This is possible only when the micromolecule consists of fewer atoms than the sulfur molecule. As we know the latter consists of 8 atoms in solutions. According to Beckman the Se molecule

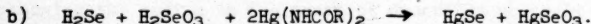
¹⁾ It is not impossible, however, that an azo compound is formed from two phenyl-nitrogen radicals when two hydrogen atoms are detached from the nitrogen.

also consists of 8 atoms in solution. This is doubtful, since if it were so selenium's higher chemical activity than sulfur would be wholly inexplicable. It must be stressed, moreover, that in the series of experiments described in the present paper the S reacted in the dissolved state, while the Se was insoluble in all the solvents I employed. The higher chemical activity of elementary Se was manifested, first, in its ability to split out hydrogen from the amino groups of aromatic amines even in the cold, yielding H_2Se . In two parallel tests the reaction of Se with aniline and with mercury acetamide in the cold was completed in 8 days, while the analogous reaction with S dragged out for several months (though the reaction ought to be promoted by the fact that the S was in the dissolved state, since both reactions were carried out in benzene).

Second, Se can decompose water at a relatively low temperature. When Se is heated with benzene containing hygroscopic water in the presence of mercury amide compounds, the reactions:



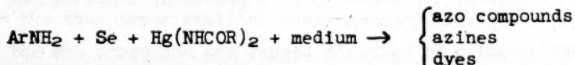
and



were completed in 4 hours in the case of mercury acetamide and in 10 days with mercury benzamide. Sulfur displays absolutely no hydrolyzing action under these conditions and, hence, does not decompose water.

Only the Se precipitated by acids as a red powder from its solutions in sulfite, caustic and cyanogen alkalies or precipitated by reducing agents from solutions of selenous acid possesses this activity. It is worthy of note that the red Se precipitated from solutions in various ways also displays varying degrees of activity. This activity disappears entirely when the red modification is heated to about 90° . It is remarkable that when the Se is heated with mercury-nitrogen compounds, its activity is retained even when it is heated to 150° .

V. Conclusion. The diagram of the dehydrogenation of primary aromatic amines with a mercury-nitrogen compound (such as mercury amide):



obviously shows that the expenditure of the amine as well as of the dehydrogenating agent (Se) in the reaction is quantitatively bound up with the consumption of the mercury amide. Since the amount of the latter may be measured quite accurately at any instant during the reaction, the rate at which the mercury amide compound is consumed indicates the overall velocity of the reaction in question as a function of: a) the composition and structure of the aromatic or heterocyclic amine; b) the composition and structure of the mercury-nitrogen compound; c) the modification of the dehydrogenating agent; and d) the medium in which the reaction is carried out.

Inasmuch as the rate at which the amine is dehydrogenated evidently depends on the strength of the bond between the hydrogen and the nitrogen in the amino group, while this bond strength, in turn, is a function of the distance between these two atoms, the relationship between the reaction velocity and the atomic distances may be determined quantitatively by comparing the dehydrogenation rate with the atomic distances in various derivatives of a single amine.

Moreover, determining the reaction velocity enables us to derive a quantitative

expression for the magnitude of the induction effect produced, *ceteris paribus*, by different substituents and their different positions with respect to the amino group. A comparison of the dehydrogenation rates of α and β naphthylamines, for example, would enable us to express the magnitude of the inductive effect of the side chain upon the bond energy of the elements in the amino group quantitatively for any given position.

The same is true, obviously, of mercury-nitrogen compounds. By changing the mercury-nitrogen compounds employed in the foregoing diagram we can judge the relationship between the reaction velocity and the distance between the mercury and nitrogen atoms from a comparison of the reaction velocity and these inter-atomic distances.

Once we have established the reaction rates for various modifications of selenium, we can select the most active one to make a comprehensive study of its properties and endeavor to establish the reason for its activity.

We know that the medium in which any given chemical reaction occurs influences the reaction rate and, sometimes the course of the reaction between the reagents. By changing the medium in the reaction described we could describe this influence quantitatively for any given medium.

Many other instances could be found of the applicability of this reaction and of its reaction velocity in solving various problems in chemical kinetics.

SUMMARY

1. When primary aromatic (and heterocyclic) amines are reacted with S or with red Se, they are smoothly converted into azo compounds, azines, and thiazine (selenazine) dyes.
2. This reaction takes place only when mercury-nitrogen compounds are involved in it (mercury substitution derivatives of amides and imides, and amines of mercury salts).
3. The parallel formation of azo compounds, azines, and dyes in this reaction is due to the tautomeric state of these mercury-nitrogen compounds.
4. The azo compounds are formed directly from the primary amine, while the dyes and azines are formed as the result of a prior transformation of the amine into a hydrazo compound, followed by the latter's rearrangement.
5. The high activity of the red modification of selenium, as compared to that of sulfur, may be due to the lower weight of its micromolecule (probably Se_2).
6. The reaction described in this report may be employed to solve various problems in chemical kinetics.

LITERATURE CITED

- [1] Cornelius, J. prak. Chem. 88, 395 (1913).
- [2] Tafel, Ber., 23, 1051 (1890).
- [3] Blancher, Ber., 28, 2354 (1895).
- [4] Reid, Am. Chem. J., 45, 43 (1923).
- [5] Goldberg, Ber., 39, 1632 (1906).
- [6] Wheeler, Am. Chem. J., 17, 398 (1895).

- [7] Thithevley, J. Chem. Soc., 79, 393 (1901).
- [8] Pinner, Ber., 16, 1654 (1888).
- [9] Buhner, Ann., 333, 292 (1904).
- [10] Comstock, Am. Chem. J., 13, 514 (1891).
- [11] Wheeler, Am. Chem. J., 23, 148 (1901).

Received October 27, 1949

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THE N-ARYL AMIDES OF HYDROXYCARBOXYLIC ACIDS
AND THEIR CONVERSION INTO HETEROCYCLIC COMPOUNDS

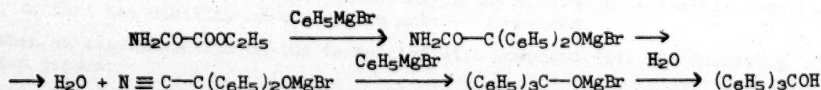
IV. THE MECHANISM INVOLVED IN THE REACTION OF ORGANOMAGNESIUM COMPOUNDS WITH THE
ESTERS OF N-ARYL-SUBSTITUTED AMIDES OF DICARBOXYLIC ACIDS

P. A. Petyunin and N. G. Panferova

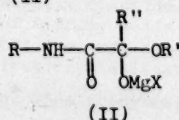
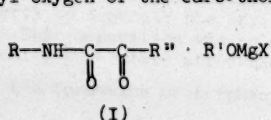
Esters of N-aryl-substituted amides of dicarboxylic acids of the $\text{RNH-CO-(CH}_2\text{)}_n\text{-COOR'}$ type contain two functional groups: the ester and the aryl amide groups. Recent papers have shed adequate light upon the mechanism involved in the reaction of esters with organomagnesium compounds [1]. As for the amide group its behavior with organomagnesium compounds is governed by the presence of substituents attached to the nitrogen, the α -carbon atom, etc.

An unsubstituted amide reacts via the addition of the alkylmagnesium halide radical to the carbonyl group [2], yielding a ketone [3]. According to Ramart [4], a trisubstituted acetamide reacts in a tautomeric (lactim) form, yielding a nitrile. Some N-disubstituted amides, as Maxim points out [5], react in such a way as to have two radicals substituted for the oxygen in the carbonyl group. When the molecule of the organic substance contains both a carbethoxy and an amido group, these groups may react individually or together, owing to their mutual influence.

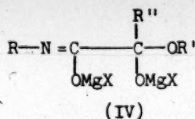
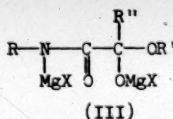
In esters of benzoylated amino acids and esters of dipeptides [6], as well as in the anilide of benzoylformic acid [7], only the carbethoxy group enters into reaction. As McKenzie and Duff [8] have shown, in an oxaminic ester (oxamethane) the carbethoxy and amido groups react simultaneously, yielding triphenylcarbinol when reacted with phenylmagnesium bromide:



Light may be shed upon the mechanism involved in the reaction of organomagnesium compounds with esters of N-aryl-substituted amides of dicarboxylic acids by a critical survey of the data in the literature, as well as by analyzing our own experimental data. When one mol of an alkylmagnesium halide was reacted with β naphthyl oxamate, we secured a substance that had the structure of a coordination compound of a halogen magnesium alcoholate with a β naphthalide of a keto acid (I) or else the structure of the addition product of an alkylmagnesium halide and the carbonyl oxygen of the carbethoxy group (II)

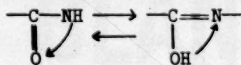


The properties of the resultant coordination compound are readily explained if we assign it the structure of a hemiketal (II). This would agree with the views of several authors regarding the mechanism involved in the reaction of organomagnesium compounds with esters [1,9], as well as with the diagram of the reduction of aldehydes and ketones by halogen magnesium alcoholates, as proposed by H. Meerwein and R. Schmidt [10]. When 2 mols of ethylmagnesium iodide are reacted with β naphthyl oxamate, one mol of ethane is liberated and a compound with the properties of a hemiketal is formed: it yields an aryl amide of a keto acid when cleaved hydrolytically. Two structures may be assigned to this compound:



The more probable of the two is Structure (IV). It explains the evolution of one mol of ethane, the hydrolytic cleavage with the formation of an aryl amide of a keto acid, and the inertness of the aryl amide group, since the latter reacts in the tautomeric (lactim) form.

Several authors have commented on the possibility of the following tautomeric transformation:

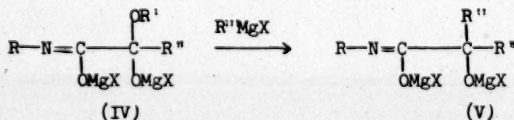


Valyashko and Bolotina [11] and Ramart-Lucas and his associates [12] have concluded that the lactim form does exist, on the basis of their determinations of the light absorption of aryl amides of carboxylic acids. Izmailsky and Smirnov [13] made a study of the color of aryl amides of nitrobenzoic acids and reached the conclusion that these compounds can exist in two forms: the lactam and the lactim.

Hence, our hypothesis that the N-aryl oxamates react with organomagnesium compounds in the lactim form is in agreement with the data in the literature.

The enolization of N-aryl oxamates is reinforced by the presence of a carbethoxy group. As we know, the carbethoxy group activates tautomeric conversions, so that the mobility of the system must be increased.

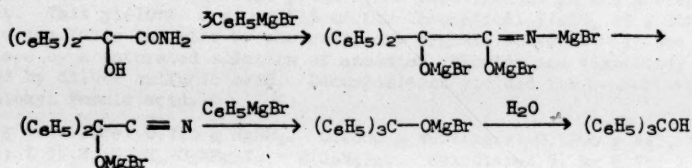
When an alkylmagnesium halide is reacted with Compound (IV) the following reaction occurs:



The magnesium halogen alcoholate (V) is insoluble in ether, but it dissolves in an excess of the organomagnesium compound. In contrast to (II) and (IV), it is readily decomposed by water and is soluble in ammonium chloride. We successfully used this property to separate the aryl amides of hydroxy acids from the aryl amides of keto acids. This separation was so simple that the aryl amides were recovered in the analytically pure state after the very first crystallization.

We regard the formation of triphenylcarbinol when phenylmagnesium bromide

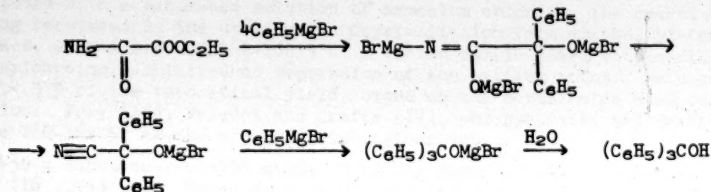
is reacted with benzilamide as a confirmation of the proposed reaction mechanism:



This reaction has not been described in the literature and is an interesting new method of synthesizing tertiary alcohols.

Our notions concerning the mechanism involved in the formation of a nitrile group from an amido group by an alkylmagnesium halide agree with those advanced by Ramart [4].

The outline proposed by McKenzie and Duff for the formation of triphenylcarbinol is in need of correction. What is improbable in this outline is the fact that the organomagnesium compound merely splits water out of the amido group. In our opinion, the oxamate reacts in the lactim form, the reaction being represented as follows:



EXPERIMENTAL

Synthesis of the addition product of $\text{C}_2\text{H}_5\text{MgI}$ and the ethyl ester of β naphthyloxaminic acid. A solution of 5 g (1 mol) of the ethyl ester of β naphthyloxaminic acid in 140 ml of anhydrous benzene was agitated vigorously while ethylmagnesium iodide, prepared from 0.5 g of magnesium and 3.2 g of ethyl iodide in 20 ml of ether, was added. The mixture warmed up slightly, and a clump of yellowish substance was thrown down. The reaction mass was then heated for 10 minutes over a boiling water bath. When the mass had cooled, the precipitate was filtered out, washed with hot benzene at first and then with ether, and dried between sheets of filter paper. This yielded 5 g of the substance, or 57.4% of the theoretical yield, based on the double compound of the ester and ethylmagnesium iodide. The substance was a slightly yellowish powder and was insoluble in water and the ordinary organic solvents. It was decomposed extremely slowly by a solution of ammonium chloride and vigorously - with the evolution of heat - by dilute sulfuric acid, the decomposition yielding the β -naphthalide of propionyl formic acid.

0.2068 g substance: 0.0610 g MgSO_4 . 0.2000 g substance: 4.81 ml 0.1 N AgNO_3 .
 Found %: Mg 5.98; I 30.5. $\text{C}_{10}\text{H}_7\text{NHCOCOC}_2\text{H}_5 \cdot \text{C}_2\text{H}_5\text{MgI}$ Calculated %: Mg 5.74; I 29.98.

Recovery of the product of the reaction of $2\text{C}_2\text{H}_5\text{MgI}$ with the ethyl ester of

beta naphthyloxaminic acid. Ethylmagnesium iodide (2 mols), prepared from 0.5 g of magnesium and 3.2 g of ethyl iodide in 20 ml of ether, was added to a solution of 2.5 g (1 mol) of the ethyl ester of β -naphthyloxaminic acid in 60 ml of anhydrous benzene. The reaction product was recovered as in the preceding experiment. This yielded 6 g, or 81% of the theoretical yield, of a substance that was insoluble in water or the customary organic solvents. It was slowly decomposed by a saturated solution of ammonium chloride and vigorously decomposed by dilute sulfuric acid. Decomposition yielded the β -naphthalide of propionyl formic acid.

0.2000 g substance: 0.710 g MgSO_4 . 0.2000 g substance: 0.1266 g AgI. Found %: Mg 7.05; I 34.2. $\text{C}_{16}\text{H}_{17}\text{O}_3\text{NMg}_2\text{I}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$. Calculated %: Mg 6.78; I 35.1.

Benzilamide. 11.4 g (1 mol) of benzilic acid was mixed with 10.4 g (1 mol) of phosphorus pentachloride. When the reaction was over, the oily liquid was triturated with solid ammonium carbonate [14]. Then the reaction product was washed with water and dried in the air. M.p. 110° . The pure amide of diphenylchloroacetic acid fuses at 115° [15].

The amide yield did not exceed 30%, since much of the diphenylchloroacetamide was saponified to benzilic acid when heated.

Triphenylcarbinol. 0.9 g of finely powdered benzilamide was added to a Grignard reagent, prepared in the usual manner from 3.5 g of bromobenzene and 0.5 g of magnesium in 15 ml of ether. The reaction was completed by heating the contents of the flask over a water bath for 30 minutes. The reaction mass was decomposed with a saturated solution of ammonium chloride, the reaction product being recovered in the usual way. Crystallization from alcohol yielded hexagonal flakes, with a m.p. of $162-162.5^\circ$. A fusion sample mixed with synthetic triphenylcarbinol exhibited no depression of the melting point. We secured 0.6 g, or 54.37% of the theoretical yield, based on the benzilamide used for the reaction. Frey [16], Friedel and Crafts [17], and Bystricki and Herbst [18] give $162-162.5^\circ$ as the m.p. of triphenylcarbinol.

0.1430 g substance: 0.4590 g CO_2 ; 0.0787 g H_2O . 0.1512 g substance: 13.9 ml CH_4 (16° , 743 mm). Found %: C 87.59; H 6.16; OH 6.48. $\text{C}_{19}\text{H}_{16}\text{O}$. Calculated %: C 87.65; H 6.2; OH 6.5.

SUMMARY

1. A mechanism is suggested for the reaction of organomagnesium compounds and esters of the N-aryl-substituted amides of dicarboxylic acids.
2. The concepts elaborated by us serve as the basis for a new outline of the reaction between oxamethane and phenylmagnesium bromide.
3. It has been found that the reaction of phenylmagnesium bromide with benzilamide involves the substitution of a radical for the amide group. This may make it an interesting new method for synthesizing tertiary alcohols.

LITERATURE CITED

- [1] A.D.Petrov, Dokl. USSR Acad. Sci. **63**, 41 (1948); I.I.Lapkin, J.Gen.Chem **17**, 1341 (1947).
- [2] F.Runge. Organomagnesium compounds, 305. United Scientific and Technical Press (1932).
- [3] C.Beis, Comptes rend., **137**, 575 (1903); Chem. Zentr., **1903**, II, 1110.
- [4] Ramart, Laclorte and Anagnostopoulos, Chem. Zentr., **1927**, II, 1566.

- [5] N.Maxim., Comptes rend., 182, 1393 (1926).
- [6] K.Thomos and F.Bettzieche, Z. physiol.Chem., 140, 244, 279 (1924); F. Bettzieche, R.Menger and K.Wolf, Z. physiol.Chem., 160, 270 (1926).
- [7] R.F.Reeies and H.G.Lindwoll, J. Am. Chem. Soc., 64, 1086, (1924).
- [8] McKenzie and Duff, Ber., 60, 1336 (1927).
- [9] A.E.Chichibabin, Jour. Russ. Chem. Soc. 37, 181 (1905).
- [10] H.Meerwein and R.Schmidt, Ann., 444, 221 (1925).
- [11] N.A.Valyashko and M.V.Bolotina, Jour. Russ. Chem. Soc. 46, 1785, 1802 (1914).
- [12] Ramart-Lucas, Wohl, Comptes rend., 196, 120 (1933); Bull. soc. chim. France 53, 14 (1933).
- [13] V.A.Izamailsky and E.A.Smirnov, J.Gen.Chem. 7, 513, 523 (1937); J.Gen Chem 8, 1730 (1938).
- [14] Klinger and Standke, Ber., 22, 1214 (1889).
- [15] H.Bickel, Ber., 22, 1538 (1889).
- [16] Frey, Ber., 28 2516, (1895).
- [17] Friedel and Crafts, Beilst., VI, 714.
- [18] Bystricki and Herbst, Ber., 35, 3137 (1902).

Received October 4, 1949.

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THE N-ARYL AMIDES OF HYDROXYCARBOXYLIC ACIDS AND THEIR
CONVERSION INTO HETEROCYCLIC COMPOUNDS

V. THE INTRAMOLECULAR CONDENSATION OF ARYL AMIDES OF BENZILIC ACID

P.A.Petyunin and I.S.Berdinsky

One of the present authors, together with Panferova [1], has established the feasibility of converting benzilanilide into 3,3-diphenyloxindole

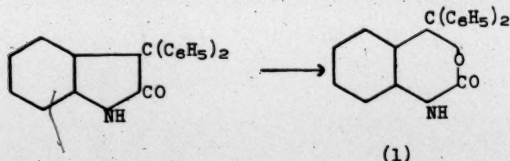
The first compounds of this kind were synthesized by Baeyer in 1885 [2] by condensing isatin with aromatic hydrocarbons in the presence of concentrated sulfuric acid. Interest in the derivatives of a 3,3-diaryloxindole has not slackened up to the present time. Wegmann and Dahn, for example, synthesized these compounds in 1946 [3] from isatin and aromatic hydrocarbons in the presence of aluminum chloride, while Sumpter and his associates [4] synthesized them from 3,3-dibromooxindole in the presence of aluminum chloride. As has been pointed out by Kaufmann [5], some derivatives of a 3,3-diaryloxindole possess marked pharmacological activity. Diacetyldiphenolisatin has been adopted by the State Pharmacopeia of the USSR under the name of Isaphenin [6]. Gabel and Zubarovsky [7] have investigated the condensation of isatin and α -naphthol in order to secure the naphthalene analog of isatin.

But up to the present time research has been done on compounds with the substituent groups in the para position in the phenyls, since the existing methods made it possible to synthesize only the compounds mentioned above. The problem of developing a method that would enable us to synthesize derivatives with the substituent groups at any desired position in the phenyls arose long ago and has become an acute one.

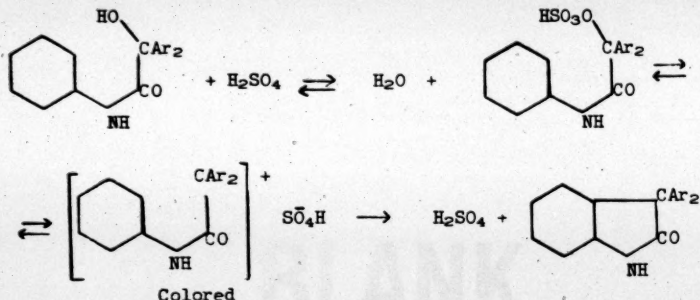
We set as our objective a comprehensive study of the intramolecular condensation of aryl amides of hydroxycarboxylic acids.

In 1912 Klinger showed that benzilanilide yields a transitory color when reacted with concentrated sulfuric acid, a substance with a m.p. of 205-210° being recovered. He failed to establish the structure of this substance, however, so that the problem of the action of sulfuric acid upon benzylanilide remained an open one. Rewes and Lindvoll [9] note that N-methylbenzylanilide yields a transient red coloration when reacted with concentrated sulfuric acid, but they made no attempt to ascertain the cause of this phenomenon.

As our researches have shown, the decolorization of colored sulfuric acid solutions is due to intramolecular condensations. In this reaction the solvent is very important. Of three solvents investigated by us: alcohol, acetone, and glacial acetic acid, the last proved to be best. The alcohol and acetone reacted with the concentrated sulfuric acid themselves, so that they are hardly suitable for use in condensation. When concentrated sulfuric acid was reacted with an acetic acid solution of benzylanilide, we secured a substance with a m.p. of 225-226°, a fusion sample of which exhibited no depression when mixed with known 3,3-diphenyloxindole. When oxidized, it yielded the 3,3-diphenylisatoic anhydride (I) mentioned in the literature [3]:



The reaction involved in the formation of 3,3-diphenyloxindole may be depicted as follows:



As this diagram indicates, the water is not directly split out during condensation, the reaction involving a stage in which a halochromic salt is formed. This condensation pattern was successfully applied to compounds of the $\text{ArNH-CO-C(OH)(C}_6\text{H}_5)_2$, where $\text{Ar} = p\text{-CH}_3\text{C}_6\text{H}_4$, $p\text{-C}_2\text{H}_5\text{OC}_6\text{H}_4$, $o\text{-CH}_3\text{OC}_6\text{H}_4$, $p\text{-(CH}_3)_2\text{NC}_6\text{H}_4$, $p\text{-BrC}_6\text{H}_4$, $\alpha\text{-C}_{10}\text{H}_7$ and $\beta\text{-C}_{10}\text{H}_7$. The properties of the resulting compounds are listed in Table 1.

Determining the optimum quantity of sulfuric acid. An accurately weighed sample of the anilide was dissolved in a fixed quantity of glacial acetic acid. Various amounts of sulfuric acid were then added, depending upon the objective of the experiment. After the reaction mass had lost its color, it was poured into twice its volume of water, the reaction product being recovered in the usual manner. The purity of the reaction product was determined from the melting point. The results are given in Table 2.

As these figures indicate, condensation takes place whenever the addition of the concentrated sulfuric acid colors the solution. No coloration was observed in Test 1, and no condensation took place, a substance with a m.p. of 171° was recovered, the m.p. of the original substance being $174\text{--}175^\circ$. The purest condensation product (m.p. 218°) was secured in Test 3. The optimum quantity of sulfuric acid may also be determined by adding it to a solution of the anilide until color no longer appears. When the condensation is to be used preparatively, it is best to determine the required quantity of sulfuric acid by the latter method. The optimum quantity of sulfuric acid is the quantity required for the complete conversion of the amount of anilide into an oxindole derivative. It is governed by the nature of the anilide, the solvent, and the reaction temperature.

Effect of temperature on the condensation rate. Two factors operate in the decolorization of the colored solutions: hydrolysis and condensation, the latter

TABLE 1

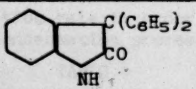
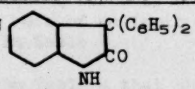
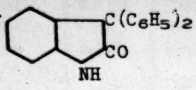
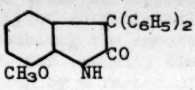
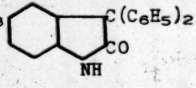
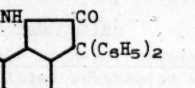
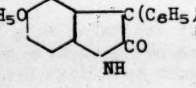
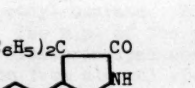
No.	Formula	Melting point	No.	Formula	Melting point
1	 <chem>C(Cc1ccc(C(=O)N)cc1)C2=CC=CC=C2</chem>	225-226°	5	 <chem>C(Cc1ccc(C(=O)N)cc1)C2=CC=CC=C2</chem>	223-225° (with decomp)
2	 <chem>BrC1=CC=C(C(=O)N)C2=CC=CC=C2</chem>	284 (with decomp)	6	 <chem>C(Cc1ccc(C(=O)N)cc1)C2=CC=CC=C2</chem>	270
3	 <chem>CC(Cc1ccc(C(=O)N)cc1)C2=CC=CC=C2</chem>	197.5 - 198.5	7	 <chem>C(Cc1ccc(C(=O)N)cc1)C2=CC=CC=C2</chem>	254
4	 <chem>CCOC(Cc1ccc(C(=O)N)cc1)C2=CC=CC=C2</chem>	250	8	 <chem>C(Cc1ccc(C(=O)N)cc1)C2=CC=CC=C2</chem>	266

TABLE 2

Test No.	2% Solution of $C_6H_5NHCOC(OH)(C_6H_5)_2$ in glacial CH_3COOH (ml)	ml of conc. H_2SO_4 used	M.p. of product	Color
1	2	0.5	171	None
2	2	1.0	210	Yellow
3	2	2.0	218	Red
4	2	3.0	215	Red
5	2	4.0	208	Red
6	2	5.0	202	Red
7	2	6.0	202	Red

TABLE 3

Test No.	Ml of anilide solution	Ml of conc. H_2SO_4	Bath temperature	Time required for color to vanish
1	1	3.5	0	4' 00"
2	1	3.5	10	2' 30"
3	1	3.5	20	1' 30"
4	1	3.5	30	1' 05"
5	1	3.5	40	0' 45"
6	1	3.5	50	0' 30"

acting more slowly than hydrolysis. We were interested in the effect of condensation alone upon the rate at which the colored solutions were decolorized. This was explored by carrying out the reaction with the optimum quantity of sulfuric acid, since then the effect of hydrolysis is excluded, the color vanishing solely as the result of condensation. The rate of condensation was determined from the rate at which the color vanished. The experiments were made with a 0.76% solution of benzylanilide in glacial acetic acid. The time required for the color to disappear was measured with a stopwatch.

The figures listed in Table 4 show that the condensation rate rises with temperature, requiring only 30 seconds at, say 50°. These results reflect the link between the reaction time and the temperature, which has enabled us to utilize this method in other cases to secure a qualitative estimate of various condensation factors.

Effect of the quantity of sulfuric acid upon the condensation rate. It has been shown above that condensation is complete only when the optimum quantity of sulfuric acid is used. When smaller quantities of sulfuric acid are used, either practically no condensation occurs at all, or part of the anilide used enters into the reaction. We investigated the effect of an excess of sulfuric acid upon the reaction rate in order to round out our study of the role of sulfuric acid in the condensation process. Our results are tabulated in Table 4.

TABLE 4

Test No.	Ml of naphthalide solution	Ml of conc. H_2SO_4	Time required for color to vanish
1	1	1.5	2' 15"
2	1	1.8	2' 30"
3	1	2.1	3' 10"
4	1	2.4	5' 33"
5	1	2.7	9' 45"
6	1	3.0	12' 50"

We see from Table 4 that the condensation rate drops off appreciably as the quantity of sulfuric acid is increased. Doubling the amount of sulfuric acid, for example, diminishes the condensation by a factor of nearly 6 (Tests 1 and 6).

EXPERIMENTAL

Ethyl ester of o-methoxyoxanilic acid. The initial substances were: 12.3 g (1 mol) of o-anisidine and 20 g (1.5 mol) of ethyl oxalate. The yield

was 0.63 g of colorless crystals with a m.p. of 245.5° . The m.p. of the o-aniside of oxalic acid is given as 245° in the literature [11]. The principal reaction product was recovered from the filtrate. Crystallization from alcohol yielded 13.7 g of colorless needles with a m.p. of 83.5° , or 61.4% of the theoretical. The ester is insoluble in water and readily soluble in most of the ordinary organic solvents. The ethyl ester of o-methoxyoxanilic acid is not described in the literature.

0.5742 g substance: 51.5 ml 0.05 N H_2SO_4 . Found %: N 6.23. $C_{11}H_{13}O_4N$. Calculated %: N 6.28.

o-Methoxyoxanilic acid. 5 g of the ethyl ester of o-methoxyoxanilic acid was heated with 200 ml of 5% sodium hydroxide until it dissolved completely. The reaction product was recovered in an analytically pure state after hydrochloric acid had been added until the reaction to Congo red was acid. Crystallization from alcohol did not raise the melting point. Colorless needles with a m.p. of 149° . The wrong figure of 159° is given as the m.p. in the literature [12].

0.2306 g substance: 11.8 ml 0.1 N H_2SO_4 . Found %: N 7.16 $C_9H_9O_4N$. Calculated %: N 7.18

o-Methoxyoxanilamide. An alcoholic solution of 3 g of the o-methoxyoxanilic ester was saturated with ammonia, yielding 1.8 g of the substance, or 81.8% of the theoretical. The amide is slightly soluble in water and in most of the ordinary organic solvents. It crystallized from a large quantity of alcohol as platelets with a m.p. of 195° . The amide of o-methoxyoxanilic acid has not been described in the literature.

0.2505 g substance: 25.6 ml 0.1 N H_2SO_4 . Found %: N 14.3 $C_9H_{10}O_3N_2$. Calculated %: N 14.43.

p-Toluidide of benzilic acid. The initial substances used were: 7 g of the ethyl ester of p-methyloxanilic acid, 31.2 g of iodobenzene, and 3.7 g of magnesium. This yielded 9.5 g of the air-dried substance, or 88.8% of the theoretical. It was crystallized from toluene in colorless needles with a m.p. of 190° . It dissolves in concentrated sulfuric acid, producing a red-brown color that vanishes rapidly.

0.1451 g substance: 4.6 ml 0.1 N H_2SO_4 . Found %: N 4.4 $C_{21}H_{19}O_2N$.
Calculated %: N 4.2

The p-toluidide of benzoic acid was secured by boiling p-toluidide of α -p-toluidinodiphenylacetic acid with concentrated sulfuric acid. M.p. 189-190° [15].

o-Aniside of benzoic acid. The o-aniside of benzoic acid was synthesized by reacting phenylmagnesium iodide (5 mols) with 7.6 g (1 mol) of the ethyl ester of o-methoxyoxanilic acid. The aniside is insoluble in water, slightly soluble in petroleum ether, and freely soluble in alcohol, ether, and benzene. With concentrated sulfuric acid it forms a red color that disappears rapidly. It crystallized from benzene as colorless needles with a m.p. of 157.5°. There is no mention of the o-aniside of benzoic acid in the literature.

0.3402 g substance: 9.62 ml 0.1 N H_2SO_4 . 0.2301 g substance: 6.7 ml 0.1 N H_2SO_4 . Found %: N 3.96, 4.08. $C_{21}H_{19}O_3N$. Calculated %: N 4.2

p-Phenetide of benzoic acid. The initial substances used were: 3.8 of magnesium, 32.5 g of iodobenzene, and 9.5 g of the ethyl ester of p-ethoxyoxanilic acid. The substance was insoluble in petroleum ether or in water, slightly soluble in carbon tetrachloride, and readily so in alcohol, acetic acid, benzene, and toluene. With concentrated sulfuric acid it produced a red-brown color that quickly turned slightly yellowish. It was purified by precipitating it from a benzene solution with petroleum ether. Colorless needles with a m.p. of 133.5 - 134.5°. The yield was 4.2 g, or 30.3% of the theoretical. The p-phenetide of benzoic acid has not been described in the literature.

0.1982 g substance: 5.98 ml 0.1 N H_2SO_4 . 0.2302 g substance: 7.1 ml 0.1 N H_2SO_4 . Found %: N 4.22, 4.32. $C_{22}H_{21}O_3N$. Calculated %: N 4.04.

The p-dimethylaminoanilide of benzoic acid was synthesized from 3.3 g (1 mol) of the ester of p-dimethylaminooxanilic acid, 11.4g (4 mols), of iodobenzene, and 1.3 g of magnesium. Crystallization from dilute alcohol yielded yellow-orange needles with a m.p. of 150-152°. The substance was recrystallized, using activated charcoal, yielding colorless needles with a m.p. of 156°. This yielded 1.2 g of the pure product, representing 26% of the theoretical yield. The substance was insoluble in water, though freely soluble in most of the ordinary organic solvents; it dissolved in concentrated sulfuric acid, turning the solution crimson, the color changing to violet, blue, and finally green. The p-dimethylaminoanilide of benzoic acid has not been described in the literature.

0.1730 g substance: 19.8 ml 0.05 N H_2SO_4 . 0.1298 g substance: 15.4 ml 0.05 N H_2SO_4 . Found %: N 8.01, 8.35. $C_{22}H_{22}O_2N_2$. Calculated %: N 8.09.

p-Bromanilide of benzoic acid. a) While a solution of 6.1 g of benzil-anilide in 75 ml of glacial acetic acid was agitated, a solution of 3.1 g of bromine in 13.5 ml of glacial acetic acid was added, yielding 6.5 g of a product, or 85% of the theoretical. Dilution of the filtrate with water yielded 0.5 g of the unreacted anilide. Crystallization from dichloroethane yielded colorless needles with a m.p. of 225-226.5°. The p-bromanilide was insoluble in water or acetic acid, though freely soluble in dichloroethane. It turned concentrated sulfuric acid red, the color vanishing rapidly.

0.1347 g substance: 3.42 ml 0.1 N H_2SO_4 . 0.2783 g substance: 0.1360 g AgBr. Found %: N 3.55; Br 20.79. $C_{20}H_{16}O_2NBr$. Calculated %: N 3.66; Br 20.92.

b) Initial substances: 2.7 g (1 mol) of the ethyl ester of p-bromoxanilic acid, 19.2 g (4.5 mols) of iodobenzene, and 1.09 g of magnesium. The yield was

¹) We secured the ester of p-bromoxanilic acid by reacting bromine with ethyl oxanilate [14].

3.4 g or 89.5% of the theoretical. It was crystallized from dichloroethane as colorless needles with a m.p. of 224-225°. A fusion sample mixed with the substance secured by brominating benzilanilide exhibited no depression of the melting point. The p-bromanilide of benzoic acid has not been described in the literature.

3,3-Diphenyloxindole. Concentrated sulfuric acid was added a little at a time to a solution of 0.5 g of benzilanilide in 5 ml of glacial acetic acid until the solution no longer turned red, a total of 5 ml of concentrated sulfuric acid being added. When the reaction mass had cooled, it was poured into twice its volume of water, the resultant precipitate being given the usual treatment. This yielded 0.46 g of air-dry product, or about 100% of the theoretical yield. Crystallization from benzene yielded colorless prisms with a m.p. of 225-226°, which agrees with the figure given in the literature for 3,3-diphenyloxindole [10].

3,3-diphenylisatic anhydride. 1.5 ml of a 50% aqueous solution of chromic anhydride was added to a solution of 1.5 g of 3,3-diphenyloxindole in 10 ml of glacial acetic acid. The reaction mass was heated over a water bath until the yellow color turned green. The reaction product was precipitated by dilution with water, and crystallized from acetic acid as colorless needles. M.p. 238-239°, in full agreement with the figure given for 3,3-diphenylisatic anhydride [3]. The yield was 0.8 g, or 51.05% of the theoretical. Concentrated sulfuric acid evolves CO₂ and colors the solution red, which is likewise characteristic of isatic anhydride.

3,3-Diphenyl-5-methyloxindole. The initial substances were: 2 g of the p-toluidide of benzoic acid, dissolved in 40 ml of glacial acetic acid and 37 ml of concentrated sulfuric acid. The yield was 1.85 g, or 97% of the theoretical. The substance was insoluble in water, slightly soluble in alcohol, toluene, and carbon tetrachloride, and freely soluble in the other organic solvents. Crystallization from toluene yielded platelets with a m.p. of 197.5 - 198.5°.

0.2317 g substance: 7.89 ml 0.1 N H₂SO₄. Found %: N 4.77. C₂₁H₁₇ON.
Calculated %: N 4.68.

3,3-Diphenyl-7-methoxyoxindole. The following substances were used for the reaction: a solution of 2 g of the p-anisidide of benzoic acid in 40 ml of glacial acetic acid, and 20 ml of concentrated sulfuric acid. The yield was 1.85 g, or 97.8% of the theoretical. The substance was insoluble in water or carbon tetrachloride, though freely soluble in alcohol, chloroform, and benzene. It was crystallized from toluene in colorless platelets with a m.p. of 270°. 3,3-Diphenyl-7-methoxyoxindole has not been described in the literature.

0.2662 g substance: 8.05 ml 0.1 N H₂SO₄. Found %: N 4.23. C₂₁H₁₇O₂N.
Calculated %: N 4.44.

3,3-Diphenyl-5-ethoxyoxindole. The 3,3-diphenyl-5-ethoxyoxindole was synthesized by adding 20 ml of concentrated sulfuric acid to a solution of 2 g of the p-phenetide of benzoic acid in 10 ml of glacial acetic acid. The yield was 1.9 g or about 100% of the theoretical. Crystallization from glacial acetic acid yielded needles with a m.p. of 250°. 3,3-Diphenyl-5-ethoxyoxindole has not been described in the literature.

0.2047 g substance: 5.94 ml 0.1 N H₂SO₄. Found %: N 4.06. C₂₂H₁₉O₂N.
Calculated %: N 4.25

3,3-Diphenyl-5-bromoxindole. Concentrated sulfuric acid was added to a suspension of 2.5 g of the p-bromanilide of benzoic acid in 75 ml of glacial acetic acid until the solution ceased being colored red-brown. The yield was 2.3 g or 96.6% of the theoretical. The substance was freely soluble in

alcohol, chloroform, and dichloroethane. It was crystallized from chloroform in colorless minute needles, with a m.p. of 284 (with decomposition). 3,3-Diphenylbromoxindole has not been described in the literature.

0.3225 g substance: 17.4 ml 0.05 N H_2SO_4 . 0.2102 g substance: 11.4 ml 0.05 N H_2SO_4 . Found %: N 3.77, 3.79. $C_{26}H_{14}ONBr$ Calculated %: N 3.85.

3,3-Diphenyl-5-dimethylamino-oxindole. 10 ml of concentrated sulfuric acid was added to a solution of 1.15 g of the p-dimethylaminoanilide of benzoic acid in 10 ml of glacial acetic acid. After the crimson color of the solution had turned to brown, the reaction mass was poured into 20 ml of water. The resultant precipitate was filtered out, washed with water and then with a 1% soda solution (to eliminate the free base), and processed thereafter as specified in the other experiments. The yield was 1 g, or 91.7% of the theoretical. The synthesized substance was insoluble in water, slightly soluble in toluene, chloroform, and dichloroethane, and readily soluble in alcohol and acetic acid. It was crystallized from alcohol as colorless needles with a m.p. of 223-225° (with decomposition). 3,3-Diphenyl-5-dimethylamino-oxindole has been synthesized by us for the first time.

0.0954 g substance: 5.62 ml 0.1 N H_2SO_4 . Found %: N 8.24. $C_{22}H_{20}ON_2$. Calculated %: N 8.54.

3,3-Diphenyl-6,7-benzoxindole. (3,3-Diphenyl- α -naphthoxindole.) (Together with N.G.Panferova.) 3,3-Diphenyl- α -naphthoxindole was synthesized by adding 45 ml of concentrated sulfuric acid to a solution of 0.4 g of the α -naphthalide of benzoic acid in 8 ml of glacial acetic acid. The yield was 0.39 g, or about 100% of the theoretical. The substance was insoluble in water, slightly soluble in alcohol and acetic acid, and readily soluble in acetone and dichloroethane. Crystallization from alcohol yielded minute needles with a m.p. of 254°. We are the first to have synthesized 3,3-diphenyl- α -naphthoxindole.

0.3550 g substance: 10 ml 0.1 N H_2SO_4 . 0.2350 g substance: 6.6 ml 0.1 N H_2SO_4 . Found %: N 4.2, 3.93. $C_{24}H_{17}ON$ Calculated %: N 4.18.

3,3-Diphenyl-4,5-benzoxindole. (3,3-Diphenyl- β -naphthoxindole). Together with N.G.Panferova.) Concentrated sulfuric acid was added to a solution of 0.4 g of the β -naphthalide of benzoic acid in 10 ml of acetic acid until the solution ceased to be colored red-brown.

The yield was 0.38 g of the substance, or nearly 100% of the theoretical yield. The synthesized substance was insoluble in water, slightly soluble in alcohol and in acetic acid, and freely soluble in acetone, chloroform, and benzene. When crystallized from alcohol, it was recovered as a fine crystalline powder (octahedrons under the microscope). M.p. 266°. 3,3-Diphenyl- β -naphthoxindole has not been described in the literature.

0.3320 g substance: 9.8 ml 0.1 N H_2SO_4 . Found %: N 4.13. $C_{24}H_{17}ON$. Calculated %: N 4.18.

SUMMARY

1. A study has been made of the intramolecular condensation of aryl amides of benzoic acid; it has been found that in this reaction 3,3-diphenyloxindole and its derivatives are produced.
2. A number of compounds not previously described in the literature has been synthesized and their properties investigated.
3. The intramolecular condensation of N-aryl amides of benzoic acid has been investigated with regard to the quantities of condensing reagents required and the reaction temperature.

LITERATURE CITED

- [1] P.A.Petyunin and N G.Panferova, J. Gen Chem. 17, 502 (1947).
- [2] A.Baeyer and M.I.Lasarus, Ber., 2637 (1885).
- [3] F.Wegmann and Dahn, Helv., 29, 415 (1946).
- [4] W.C.Sumpter, M.Miller and L.M.Hendrick, J.Am.Chem.Soc. 67, 1656 (1945).
- [5] H.P.Kaufmann, Z.Ang. Ch., 40, 831 (1927).
- [6] State Pharmacopeia of the USSR, 8th ed., p.275. State Medical Press (1946).
- [7] Yu. O.Gabel and V.M.Zubarovsky, J.Gen.Chem. 7, 305 (1937).
- [8] H.Klinger, Ann., 389, 256 (1912).
- [9] R.F.Reves and H.G.Lindwoll, J.Am.Chem Soc., 64, 1086 (1942); C.A., 4114 (1942).
- [10] F.Wegmann and Dahn, Helv., 29, 429 (1946).
- [11] Bischoff, Ber., 39, 3973 (1906).
- [12] Anselmino, Chem. Zentr., 1906, 1, 753.
- [13] Klinger, Ann., 389, 261 (1912).
- [14] Klinger, Ann., 184, 267 (1876).

Received October 10, 1949.

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MESO DERIVATIVES OF ACRIDINE

XXI. THE REACTION OF ACRIDINES WITH BISULFITE

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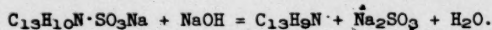
Grebe [1] was the first to investigate the reactions of acridine with sulfuric acid and sulfates, and two compounds were described by him. One of them, which was prepared by reacting sulfuric acid with acridine and was a red, slightly soluble substance, had the composition of a neutral sulfite of acridine: $(C_{13}H_9N)_2 \cdot H_2SO_3$. The other substance, synthesized by reacting sodium sulfite with acridine hydrochloride, was assigned the formula of $C_{13}H_9N \cdot SO_3HNa$ by Greebe, who regarded it as the addition product of bisulfite and acridine without undertaking a detailed study of its structure. In contrast to the former compound, this substance was colorless and readily water soluble. Subsequently E.Wirth and K. Lehmstedt [2] found that the latter compound was formed when acridine was reacted with a bisulfite solution. These investigators concluded that, in contrast to pyridine and quinoline bases, which constitute unstable saltlike compounds with bisulfite, the reaction of bisulfite with acridine results in the formation of the sodium salt of 9,10-dihydroacridine-9-sulfonic acid or of acridan-9-sulfonic acid. The principal reason underlying this concept of the structure of the reaction product of acridine and bisulfite was its colorlessness, which is not typical of acridine salts, usually colored. Moreover, the authors cited felt that only those acridines could react with bisulfite that had an unsubstituted hydrogen atom attached to the meso carbon atom, although they cited no experimental evidence in support of this assertion, inasmuch as they had explored only the single reaction of bisulfite with acridine.¹

Acridan-9-sulfonic acid proved to be a compound with singular properties, differing from those of ordinary sulfo acids. In aqueous solutions or when moist, it was readily and rapidly oxidized to the "red acridine sulfite" mentioned in Grebe's paper: $2C_{13}H_{10}N \cdot SO_3Na + O = (C_{13}H_9N)_2 \cdot H_2SO_3 + Na_2SO_4$, which in turn reacted with the neutral sodium sulfite, being converted into acridan-9-sulfonic acid. Moreover, Wirth and Lehmstedt found that, in contrast to ordinary sulfo acids, in which the replacement of the sulfo group by a cyanogen group is achieved with difficulty, acridan-9-sulfonic acid is converted into 9-cyanacridine when heated for half an hour over a water bath with an aqueous-alcoholic solution of potassium cyanide.

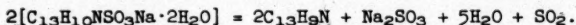
In our research into the reactions of acridine, 2-methylacridine, and 2-methoxy-acridine with sodium bisulfite, we have found that in the simplest case a substance is formed that is identical with Lehmstedt's and Wirth's sodium salt of acridan-9-sulfonic acid, the corresponding analogs being formed from the substituted acridines. The products were crystalline, colorless compounds that were readily soluble in water and slightly soluble in organic solvents, and unstable in aqueous solutions. Their solutions were oxidized after standing for a short time, yielding colored, insoluble compounds. But these solutions could

1) This rule, which was not confirmed experimentally by Wirth and Lehmstedt, certainly requires supporting proof, since we have found, for example, that 2,7-dimethylacridine does not form a compound analogous to acridan-9-sulfonic acid when reacted with bisulfite, even though its meso position is open.

be kept indefinitely in closed vessels containing bisulfite. In contrast to the salts of ordinary sulfo acids, the sodium salts we had synthesized were instantaneously decomposed into the respective acridine derivative and sodium sulfite when reacted with dilute alkalis or ammonia, even in the cold. This reaction, which is the basis for the method we have used to analyze the compounds we have synthesized for their sulfur content, is a quantitative one, the simplest example being:

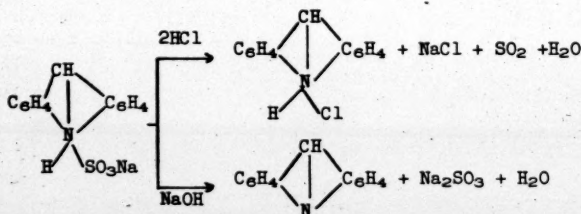


The solid salts are decomposed by mineral acids, yielding the respective acridine salts and liberating sulfur dioxide. The behavior of the synthesized salts when heated is interesting. When heated to a high enough temperature in a suitable organic solvent, say toluene, they are quantitatively decomposed into the respective acridine derivative, neutral sodium sulfite, water, and sulfur dioxide. This transformation may be represented by the following equation for the simplest case:

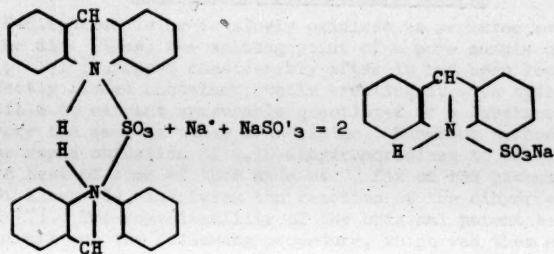


The quantitative nature of this thermal decomposition made it possible to utilize it as a method of determining the water of crystallization and of constitution (and the sulfur dioxide) in the synthesized crystalline salts. In contrast to the salts of ordinary sulfo acids, the salts we synthesized were converted into the respective 9-cyanacridines when they were heated for even a short time with an aqueous-alcoholic solution of potassium cyanide. The resulting 9-cyanacridine, 2-methyl-, and 2-methoxy-9-cyanacridines were identical with the compounds described by us in one of our previous papers [3].

All these properties of the compounds we have synthesized are inexplicable or hard to explain if we imagine their structure to be that of salts of acridan-9-sulfonic acid, which forces us to search for some other structure of these compounds that satisfies the properties described. A structure that does so is, apparently, the structure of sulfites of the sodium-acridinium compounds that are isomers of the salts of acridan-9-sulfonic acids. The behavior of the synthesized salts when exposed to heat or the action of acids and alkalis, and their ready oxidizability in aqueous solutions, may be explained satisfactorily if they are regarded as double sulfites of sodium and acridinium (an analog of tetrasubstituted ammonium). The action of alkalis and acids may be readily explained by the following equations:



This view of the structure of the compounds synthesized as sodium-acridinium sulfites makes some of their properties observed by previous researchers readily understandable. The formation of Lehmstedt's and Wirth's sodium salt of acridan-9-sulfonic acid by the action of neutral sodium sulfite on Grebe's "red acridine sulfite" is explained simply as follows:



Without regarding the question of the structure of the products of the reaction of NaHSO_3 with the acridones as definitely settled by our experiments, we are inclined to believe that the properties of the compounds in question are most satisfactorily explained at the present stage of our knowledge of their nature by the proposed concept of their structure as double sulfites of sodium and acridiniums.

The general method employed to synthesize the acridines used as the initial substances is the reduction of acridones, the most satisfactory results being secured when the acridones are reduced with sodium amalgam [4] or metallic sodium [5] in boiling alcohol. In such a reduction acridine is produced, together with a large quantity of 9,10-dihydroacridine and a small quantity of 9,10,9',10'-tetrahydro-9,9'-biacridyl, which is disproportionated into acridine and 9,10-dihydroacridine only when heated to high temperature. The utilization of the foregoing method therefore required the elaboration of conditions that would ensure a minute yield of the biacridyl and a method for oxidizing the 9,10-dihydroacridones to acridines.

EXPERIMENTAL

Acridine and 9,10-Dihydroacridine

240 g of 2% sodium amalgam was added in the course of $1\frac{1}{2}$ - 2 hours, with efficient mechanical stirring, to a suspension of 8 g of acridone in 300 ml of 95% ethyl alcohol heated to boiling, after which the heating was continued for another 4-5 hours. The mercury and the insoluble precipitate of 9,10,9',10'-tetrahydro-9,9'-biacridyl were filtered out of the hot solution, and all the solvent was driven out of the filtrate. The solid residue left after this driving off was extracted with water to eliminate the alkali and then with hot dilute hydrochloric acid. The acid extract was separated from the 9,10-dihydroacridine insoluble in acids and then neutralized with ammonia, precipitating acridine, which had a m.p. of 107° without purification. The acridine yield averaged 2.8 g or 38% of the theoretical. The precipitated 9,10-dihydroacridine had the appearance of adhering dark-green clumps. The clumps were treated with dilute ammonia to secure it in the pure state, the resulting finely-crystalline, brownish-yellow powder being recrystallized from diluted alcohol, after which its m.p. was 171° . The average yield of the 9,10-dihydroacridine was 4.4 g, or 59% of the theoretical. Reduction of the insoluble precipitate yielded, in addition to the acridine and the 9,10-dihydroacridine, some 0.4-0.45 g of 9,10,9',10'-tetrahydro-9,9'-biacridyl, which fused at $213-214^\circ$ after recrystallization from an aniline-benzene mixture.

Oxidation of 9,10-Dihydroacridine

The 9,10-dihydroacridine is slowly oxidized to acridine even when it is exposed to the air. Thus, the melting point of a pure sample of 9,10-dihydroacridine (m.p. 171°) dropped considerably after it had been kept for two months in an imperfectly closed container, while treating it with hydrochloric acid made it possible to extract measurable quantities of a substance, all of whose properties were the same as those of acridine. Numerous methods have been proposed for the rapid oxidation of 9,10-dihydroacridines to the respective acridines [6]. A test of some of them made us fix on the patent method of W. Perkin and G. Klems [7], involving the reaction of the dihydroacridines with nitrous acid [7]. The unavailability of the original patent text made it necessary to work out the following procedure, which was then employed in all the tests.

5.4 g of 9,10-dihydroacridine was dissolved by heating it in 170-180 ml of 80% acetic acid. The solution was chilled to from 0° to -3°, and a cold solution of 2.1 g of sodium nitrite was added, with constant stirring, the temperature of the mixture not being allowed to exceed 5°. Everything dissolved after 10 minutes had elapsed, and oxidation was complete. The solution was chilled and then cautiously neutralized with ammonia. The tar that settled out at the beginning of neutralization was filtered out, and ammonia was added to the filtrate until a permanent odor appeared. The resultant acridine precipitate (4.5-4.8 g) was purified with the minimum losses by converting it into the sodium salt of acridan-9-sulfonic acid by the method described below and decomposing the latter with an alkali solution. This yielded 4.4-4.7 g of acridine (84-90% of the theoretical), with a m.p. of 107°.

The Sulfite of Sodium-Acridinium, $C_{13}H_{10}NO_3SNa \cdot 2H_2O$

1.8 g of acridine, 1.9 g of sodium bisulfite, and 0.8 g of sodium sulfite were dissolved by heating them in 30 ml of water. The hot solution was filtered, the minute colorless needles of sodium-acridinium sulfite that settled out of the cooling solution being suction filtered out carefully and washed, at first with a small quantity of 40-50% alcohol, and then with 95% alcohol, after which they were air-dried. The yield of sodium-acridinium sulfite was 2.55-2.60 g, or 80-82% of the theoretical. Decomposition of the mother liquor with an alkali yielded about 0.2 g of acridine (m.p. 107°). The sodium-acridinium sulfite, synthesized by the method described, was absolutely pure in most instances, and could be analyzed directly. It crystallized with two molecules of water, which it gave up when dried at 90-95°. As the water of crystallization was driven off, the salt slowly decomposed, sulfur dioxide being liberated, and acridine and sodium sulfite being formed. This transformation is smooth and lossless when the salt was heated in boiling toluene, so that it may be employed for the quantitative determination of water and of half the total sulfur (as SO_2). The following method was employed to analyze the other investigated sodium sulfites and substituted acridines.

A sample of the sodium-acridinium sulfite (1-2 g) was placed in a weighed 100-ml round-bottomed flask and mixed with 50 ml of anhydrous toluene. The flask was connected to a reflux condenser, and the contents were boiled for 30 minutes; then all the toluene was driven off (the residue in a low vacuum), and the flask was weighed with its dry residue. The results of analysis satisfied the foregoing decomposition reaction.

1.5678 g subs.; loss in weight 0.3710 g. Found %: H_2O and SO_2 23.66. $C_{13}H_{10}O_3NSNa$. Calc. %: H_2O and SO_2 24.15.

The resulting salt was soluble in water, though insoluble in organic solvents. The aqueous solutions are highly unstable, a red amorphous deposit settling out after a relatively short time. Solutions of the salt keep indefinitely in closed containers in the presence of bisulfite. Acridine is produced when the salt solutions are acted upon by caustic alkalies. Mineral acids evolve sulfur dioxide from the solid salt, an acridine salt being formed. We employed the following method to determine the sulfur in the resulting salt, as well as in the other sodium-acridinium sulfites. A solution of 0.2-0.4 g of sodium-acridinium sulfite was alkalized with a slight excess of caustic alkali, the precipitated acridine being filtered out and washed. The filtrate, whose volume must not exceed 100 ml, was slowly poured, with frequent agitation, into a flask containing a measured volume of a 0.1 N solution of iodine acidulated with concentrated hydrochloric acid. The flask was closed with a ground-glass stopper, the excess iodine being back-titrated with hyposulfite containing starch after 5 minutes of agitation.

0.3913 g subs.: 24.33 ml 0.1 N. I_2 . 0.2592 g subs.: 16.22 ml 0.1 N I_2 . Found %: S 9.97, 10.03. $C_{13}H_{10}O_3NSNa \cdot 2H_2O$. Calc. %: S 10.05.

2-Methylacridine and 2-Methyl-9,10-dihydroacridine

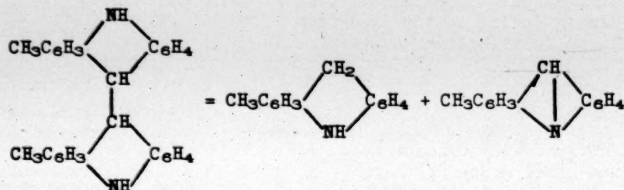
290 g of 2% sodium amalgam was added in small batches in the course of 2 hours, with constant stirring, to a suspension of 8 g of 2-methylacridone in 300 ml of 95% ethyl alcohol heated to the boiling point. After all the amalgam had been added, heating was continued for another 4-5 hours, after which the insoluble precipitate of 2,2'-dimethyl-9,10,9',10'-tetrahydro-9,9'-biacridyl and the mercury were filtered out of the hot solution of reduction products, and all the solvent was driven out of the filtrate. The solid residue was first extracted with water and then with an excess of hot dilute hydrochloric acid, the 2-methyl-acridine dissolving and thus being separated from the 2-methyl-9,10-dihydroacridine, which was insoluble in acids. The 2-methylacridine was precipitated by ammonia or caustic alkalies from the acid solution as a nearly colorless powder; it was a wholly pure product that fused at 134-134.5°. Its yield averaged 3.5 g, or 47% of the theoretical. The 2-methyl-9,10-dihydroacridine isolated from the acid solution consisted of dark-green, greasy cubes; in that state it could be oxidized to 2-methylacridine without special purification. When treated with ammonia, it was converted into a brownish-yellow powder that had a m.p. of 157° after recrystallization from dilute alcohol. The yield of the pure 2-methyl-9,10-dihydroacridine averaged 3 g, or 40% of the theoretical.

Oxidation of 2-methyl-9,10-dihydroacridine to 2-methylacridine occurred slowly when it was exposed to the air for a long time. This transformation takes place more quickly when oxidizing agents are used. The results were good when the method described in the oxidation of 9,10-dihydroacridine was used, employing 5.8 g of 2-methyl-9,10-dihydroacridine instead of the quantity indicated. The 2-methylacridine thus synthesized could be purified via sodium-2-methylacridinium sulfite, the yield of pure 2-methylacridine, with a m.p. of 134°, being 5.2-5.4 g, i.e., 92-96% of the theoretical, based on the oxidation of 2-methyl-9,10-dihydroacridine.

Alongside the 2-methylacridine and the 2-methyl-9,10-dihydroacridine, the reduction of 2-methylacridone yielded about 0.5 g (some 5% of the theoretical) of 2,2'-dimethyl-9,10,9',10'-tetrahydro-9,9'-biacridyl. The m.p. of the latter exceeded 290° after purification by recrystallization from dimethylaniline and benzene.

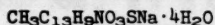
0.1124 g subs.: 7.2 ml N_2 (18°, 758, mm). Found %: N 7.33. $C_{28}H_{24}N_2$. Calc. %: N. 7.22.

When 2,2'-dimethyl-9,10,9',10'-tetrahydro-9,9'-biacridyl was heated above its melting point, it was disproportionated into equimolecular quantities of 2-methylacridine and 2-methyl-9,10-dihydroacridine:



3.5 g of 2,2-dimethyltetrahydrobiacridyl was placed in a hard glass tube sealed at once and heated over an open flame for 1 hour. The resultant mixture of 2-methylacridine and 2-methyl-9,10-dihydroacridyl was separated by treating it with dilute hydrochloric acid. This yielded 1.55 g of 2-methylacridine (89% of the theoretical) and 1.65 g of 2-methyl-9,10-dihydroacridine (93% of the theoretical). These substances were identical with the corresponding products of the reduction of 2-methylacridone (mixed fusion tests).

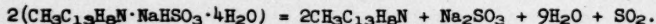
The Sulfite of Sodium-2-methylacridinium



1.9 g of 2-methylacridine, 1.8 g of sodium bisulfite, and 0.8 g of sodium sulfite were dissolved by heating them in 15 ml of water over a water bath. The solution was filtered, and the chilled filtrate was saturated with sodium chloride. After some time had elapsed a finely crystalline, nearly colorless precipitate of the sulfite of sodium-2-methylacridinium settled out. The latter was carefully suction - filtered out of the mother liquor, washed with 1-2 ml of ice water at first and finally with alcohol and ether. The yield of the sulfite of sodium-2-acridinium, which was a completely pure product, was 2.85 g, or 75% of the theoretical. About 0.45 g of 2-methylacridine could be recovered by alkalinizing the mother liquor.

0.3471 g subs.: 18.21 ml 0.1 N I_2 . 0.3205 g subs.: 17.04 ml 0.1 N I_2 . Found %: S. 8.51, 8.52. $C_{14}H_{12}O_3\text{NSNa} \cdot 4\text{H}_2\text{O}$. Calc. %: S 8.68.

The synthesized salt was insoluble in organic solvents, but was very readily soluble in water. The aqueous solutions were rose-colored or flesh-red, a dark-green amorphous precipitate settling out when they were allowed to stand. When stored in the presence of bisulfite the solutions keep, without changing. The sulfite of sodium-2-acridinium behaves like the sulfite of sodium-acridinium in the presence of alkalis or acids. When it was heated (say, by boiling with toluene), it decomposed quantitatively as follows:



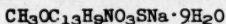
0.9034 g subs.: loss in weight 0.2778 g. Found %: H_2O and SO_2 30.75. $C_{14}H_{12}O_3\text{NSNa} \cdot 4\text{H}_2\text{O}$. Calc. %: H_2O and SO_2 30.63.

2-Methoxyacridine

In contrast to the preceding instances of the reduction of acridones, the reduction of 2-methylacridone by sodium amalgam is less smooth, resulting in the formation of large quantities of a substance whose properties resemble those of the tetrahydro-9,9'-biacridyl mentioned above, which apparently is a dimethoxy substitution derivative of this series of compounds. Good results can be obtained by employing the following modification of the method of W. Borsche, F. Runge, and W. Trautner [8].

6 g of sodium were added to a boiling solution of 3 g of 2-methoxyacridone in 150 ml of 95% alcohol, and the solvent was driven off after the sodium had dissolved. The remaining solid mixture of reduction products was dissolved (after having been extracted with water containing alkali) in 70-80 ml of hot 80% acetic acid. The hot solution was filtered, the filtrate being chilled to 0-5° and vigorously stirred while a cold solution of 1.0 g of sodium nitrite in 10 ml of water was added. Oxidation was complete in 10 to 15 minutes. The cold solution was cautiously neutralized with ammonia until single flocs of a precipitate contaminated with tarry products appeared. The liquid was filtered, and then the neutralization with ammonia was completed (a manifest odor of ammonia). The crude 2-methoxyacridine (m.p. 88-94°) was purified by converting it into the sulfite of sodium-2-methoxyacridinium and decomposing the latter with ammonia. The yield of pure 2-methoxyacridine, with a m.p. of 103°, was 1.8-1.9 g or 65-68% of the theoretical.

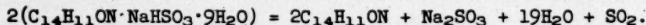
The Sulfite of Sodium-2-methoxyacridinium



1 g of 2-methoxyacridine, 1 g of sodium bisulfite, and 0.5 g of sodium sulfite were dissolved by heating them in 10 ml of water over a water bath. The solution was filtered, and the filtrate saturated in the cold with sodium chloride. After a fairly long time had elapsed, the nearly colorless flocs of the sulfite of sodium-2-methoxyacridinium settled out. The latter were filtered out and washed, at first with 30-40% alcohol, then with 95% alcohol, and finally with ether. The resulting salt required no further purification. Its yield totaled about 1.6 g, or 70% of the theoretical.

0.1296 g subs.: 5.68 ml 0.1 N I_2 . 0.2133 g subs.: 9.25 ml 0.1 N I_2 . Found %: S 6.87, 6.80. $\text{C}_{14}\text{H}_{12}\text{O}_4\text{NSNa}\cdot 9\text{H}_2\text{O}$. Calc. %: S 6.74.

The resultant sodium salt was very highly soluble in water, though insoluble in organic solvents. Its aqueous solutions had the same properties as those of the other sodium-acridinium sulfites, while its behavior with acids and alkalis resembled that of the latter sulfites. It evolved water and sulfur dioxide when boiled in toluene, decomposing to 2-methoxyacridine and sodium sulfite:



1.2354 g subs.: loss in wt. 0.4485 g. Found %: H_2O and SO_2 36.3.
 $\text{C}_{14}\text{H}_{12}\text{O}_4\text{NSNa}\cdot 9\text{H}_2\text{O}$. Calc. %: H_2O and SO_2 36.0.

SUMMARY

It has been found that the reaction of acridine, 2-methylacridine, and 2-methoxyacridine with sodium bisulfite yields compounds, the simplest of which is identical with Lehmstedt's and Wirth's sodium salt of acridan-9-

sulfonic acid.

Investigation of the properties of the compounds synthesized has established that they are instantaneously decomposed to acridine and neutral sodium sulfite by the action of dilute alkalies, to a salt of acridine and sulfur dioxide by the action of mineral acids, and are quantitatively decomposed by heating to as low as 100-110° into acridine, neutral sodium sulfate, sulfur dioxide, and water.

The combination of all these properties forces us to assign the structure of double sulfites of sodium and acridiniums (sodium-acridinium sulfites) to the compounds synthesized.

The reduction of acridone, 2-methylacridone, and 2-methoxyacridone by sodium and sodium amalgam in alcohol, the separation of the reduction products, and the oxidation of the 9,10-dihydroacridines to acridines have been described.

LITERATURE CITED

- [1] C. Graebe, Ber., 16, 2830 (1883).
- [2] E. Wirth, German Patent 440771 and 440772 (Frdl., 15, 342 and 344); K. Lehmstedt and E. Wirth, Ber., 61, 2046 (1928).
- [3] N. Drozdov and O. Cherntsov, J. Gen. Chem., 14, 181 (1944).
- [4] Cf: F. Ullmann and R. Maag, Ber., 40, 2521 (1907) and R. Reed, J. Chem. Soc., 1944, 679.
- [5] Cf: Graebe and Lagodzinski, Ann., 276, 48 (1893); H. Jensen and M. Friedrich, J. Am. Chem. Soc., 49, 1050 (1927).
- [6] E.g. cf: C. Graebe, Ann., 279, 269 (1894); F. Ullmann, Ber., 36, 1017 (1903); W. Borsche, F. Runge and W. Trautner, Ber., 66, 1316 (1933); H. Jensen and M. Friedrich, J. Am. Chem. Soc., 49, 1050 (1927).
- [7] W. Perkin and G. Klems, British Patent 214756 Chem. Zentr. 1927, II, 1308.
- [8] W. Borsche, F. Runge and W. Trautner, Ber., 66, 1316 (1933).

Received October 24, 1949.

SYNTHESES OF ANTHELMINTHICS OF THE COUMARIN SERIES

I. Ya. Postovsky and M. A. Panyukova

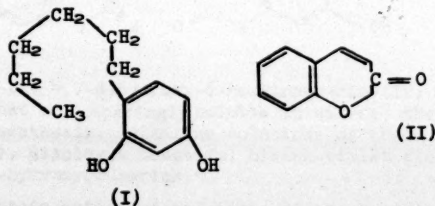
Researches on various lactones and derivatives of polyhydric phenols (phloroglucinol and resorcinol) occupy a special place in the work on the synthesis of anthelmintic compounds. In this connection we have synthesized compounds that are both lactones and phenol derivatives, in the expectation that they would display considerable anthelmintic activity.

The lactone ring is a typical group in the molecule of santonin, a natural, highly active anthelmintic. Numerous syntheses of various lactones have still failed to disclose any new highly active vermifuge.¹

Derivatives of the polyhydric phenols, such as phloroglucinol, are the active principle in the extract of the male fern (*Aspidium filixmas*), which has long been used as a vermifuge [2]. The filixic acid, albaspidin, and flavaspidic acid recovered from these extracts are, according to Bohm [3], methylene-bis derivatives of phloroglucinol.

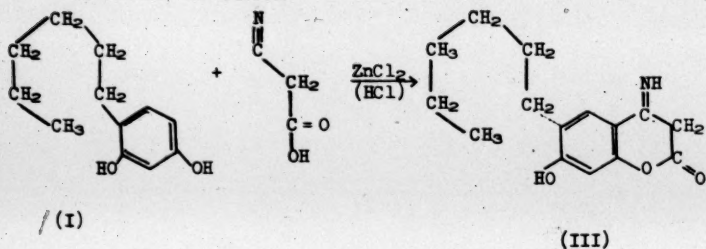
The researches of P. Karrer [4], undertaken in connection with Bohm's investigations, have shown that the methylene-bis derivatives of phloroglucinol are slightly anthelmintic, being inferior in this respect to the phloroglucinol derivatives that have no methylene bridge. Various derivatives of resorcinol also possess anthelmintic properties. Hexylresorcinol (I), for instance, has been utilized as a vermifuge for invasions of ascarids and ancylostomes [5].

In our research we have synthesized compounds possessing the hexylresorcinol (I) group and containing the lactone ring of coumarin (II). We selected this lactone because coumarin itself exhibits a narcotic action upon rainworms [6], evidence of potential vermifuge properties of coumarin [7] and its derivatives.

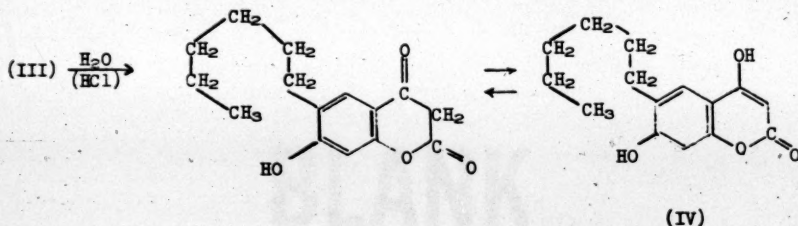


These compounds were synthesized by condensing hexylresorcinol (I) with cyanacetic acid (or its ester). The reaction yielded the ketimine of a coumarin compound (2-oxo-4-imino-6-hexyl-7-hydroxychroman (III)), the yield being 50% of the theoretical.

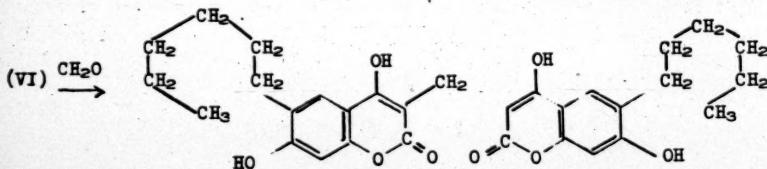
1) E.g., of the paper by S. I. Sergievskaya and A. V. Danilova on the synthesis of derivatives of tetrahydronaphthalene with a lactone ring [1].



When the ketimine (III) was hydrolyzed with hydrochloric acid, a satisfactory yield of 4,7-dihydroxy-6-hexylcoumarin (IV) was obtained:



The products synthesized contained the reactive methylene group (at the 3 position) and react smoothly with formaldehyde in alcoholic solution yielding methylene-bis compounds such as benzotetronic acid (4-hydroxycoumarin) [8] yields the so-called "dicoumarol" (methylene-bis-4-hydroxycoumarin) [9].



The ketimine (III) and the 4,7-dihydroxy-6-hexylcoumarin (IV) are readily crystallizable substances that are sparingly soluble in water; they burn the tongue and cause a slight anesthesia. Alkaline solutions of these substances, especially of Substance (IV), display a beautiful bluish-violet fluorescence, such as characterizes the 7-hydroxycoumarins.¹

A test of the anthelmintic action of solutions of the ketimine and of 4,7-dihydroxy-6-hexylcoumarin in a physical liquid (3 mg of the substance per 100 ml of physiological solution) on rainworms indicated considerable activity, about equal to the activity of hexylresorcinol. Experiments on cats,² showed

1) This test was performed by N. I. Efimov, to whom we wish to express our thanks.

2) V. L. Zolotov and L. P. Zharova have employed this property of the synthesized substances for use as acid-basic indicators in the titration of turbid and colored liquids [10].

that these compounds were not tolerated too well by animals in doses of 0.1-0.2 g, causing hyperemia of the intestinal tract, so that the use of large doses was inadvisable. In the doses specified the synthesized compounds (III) and (IV) did not display the expected anthelmintic action.

EXPERIMENTAL

1. Synthesis of 2-oxo-4-amino-6-hexyl-7-hydroxychroman (III). 48.5 g (0.25 mol) of hexylresorcinol (m.p. 67-69°), 21.3 g (0.25 mol) of cyanacetic acid, 150 ml of absolute ether, and 14.5 g of freshly fused zinc chloride, ground to a powder, were placed in a 250-ml round-bottomed three-necked flask fitted with a liquid-seal mechanical stirrer, a condenser and a gas inlet tube. The flask was placed in an ice-water bath, and a strong current of hydrogen chloride was passed through the suspension while the stirrer was running. As the reaction proceeded, the hexylresorcinol and the zinc chloride dissolved, the solution turning a dark-cherry color. After the hydrogen chloride had been passed through the reaction mass for six or seven hours, it turned cloudy and separated into two layers, ethereal and oily. The ether was driven off over a water bath, the thick, dark cherry-red oil remaining in the flask being treated with about 600 ml of water. Adding the water and stirring for about an hour caused the oil to crystallize gradually into a pinkish greasy paste. After being squeezed out on a plate the ketimine (III) was a nearly colorless powderlike product (m.p. 138-140°). The yield was 50 g. Recrystallization by boiling it in three times its weight of alcohol containing activated charcoal yielded 30 g of the substance as orthogonal platelets with a m.p. of 171-172°. The yield was 46% of the theoretical. Recrystallization from alcohol yielded 18 g of a substance with a constant m.p. of 175-176°. The substance fluoresces beautifully at a pH of 5-6 and upward.

An alcoholic solution of the ketimine (III) reacts readily when heated with a 35% aqueous solution of formaldehyde, yielding 80-90% of methylene-bis-(2-oxo-4-amino-6-hexyl-7-hydroxychroman) as minute colorless, silky needles, growing in clusters. M.p. 184-185°

4.13 mg substance: 0.196 ml N₂ (17°, 750 mm); 5.09 mg substance: 0.235 ml N₂ (17° 750 mm). Found %: N 5.51, 5.35. C₁₅H₁₉NO₃ Calculated %: N 5.36.

3.35 mg substance: 0.1548 ml N₂ (17° 750 mm); 5.21 mg substance: 0.245 ml N₂ (17°, 750 mm). Found %: N 5.49, 5.46. C₃₁H₃₉N₂O₆. Calculated %: N 5.24.

2. Synthesis of 4,7-dihydroxy-6-hexylcoumarin (IV). 5.2 g (0.02 mol) of the ketimine (III) and 150 ml of 25% hydrochloric acid were placed in a round-bottomed flask fitted with a reflux condenser and heated for eight hours over a boiling water bath. The ketimine dissolved after 10 to 15 minutes of heating, forming a light cherry-red oil. As heating continued, the oil slowly turned into a crystalline product, which was filtered out, washed with 100 ml of water, and pressed on a clay plate to remove all traces of oily impurities. This yielded 5 g of a substance that crumbled into powder. After recrystallization from three times its weight of alcohol containing activated charcoal the product consisted of microscopic orthogonal platelets in clusters. M.p. 220-221°; yield 3 g, or 58% of the theoretical.

Recrystallization from alcohol yielded 1.8 g of a substance with a constant m.p. of 228-229°. 4,7-Dihydroxy-6-hexylcoumarin is freely soluble in the usual organic solvents.

0.0342 g substance: 0.0850 g CO₂; 0.0212 g H₂O. Found %: C 67.78; H 6.93. C₁₅H₁₈O₄. Calculated %: C 68.68; H 6.92.

The lower percentage of carbon in the recrystallized product is apparently due to the difficulty of eliminating the contaminating dihydroxyhexylacetophenone, formed when the alcoholic solution of the substance was boiled.

An alcoholic solution of 4,7-dihydroxy-6-hexylcoumarin (IV) reacted readily with 35% aqueous solution of formaldehyde, producing a nearly quantitative yield of methylene-bis-(4,7-dihydroxy-6-hexylcoumarin), consisting of minute needles with a m.p. of 274-275°. The product was analyzed without preliminary purification, owing to its sparing solubility in most organic solvents.

0.0414 g substance: 0.1052 g CO₂; 0.0252 g H₂O. Found %: C 69.30; H 6.81. C₃₁H₃₆O₆. Calculated %: C 69.42; H 6.71.

SUMMARY

In a search for new anthelmintics new coumarin compounds have been synthesized: 2-hydroxy-4-imino-6-hexyl-7-hydroxychroman [the ketimine (III)] and 4,7-dihydroxy-6-hexylcoumarin (IV). These compounds produced hyperemia of the intestinal tract when administered in doses of 0.1 - 0.2 g to cats, without displaying any marked anthelmintic properties.

LITERATURE CITED

- [1] S. I. Sergievskaya and A. V. Danilova, *J. Gen. Chem.* **16**, 1077 (1946).
- [2] M. P. Nikolaev. *Textbook of pharmacology*, 350. State Medical Press (1948).
- [3] R. Bohm, *Ann.*, **318**, 271 (1901).
- [4] P. Karrer, *Helv. Chim. Acta*, **2**, 473 (1919).
- [5] M. D. Mashkovsky. *Handbook of new therapeutic preparations*, p. 184. State Medical Press, (1948).
- [6] E. Spath, *Ber.*, **70**, 116 (1937).
- [7] R. E. Shults and N. P. Shikhobalova, *Med. Parasitol.* **3** (6), 535 (1934).
- [8] R. Anschutz, *Ann.*, **367**, 212 (1909).
- [9] M. A. Stohmann, Ch. F. Ruebner, R. P. Link, *J. biol. chem.*, **138**, 513 (1941).
- [10] V. L. Zolotovin and L. P. Zharova, *Factory Lab.*, 1951, No. 6, 680.

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Received November 12, 1949.

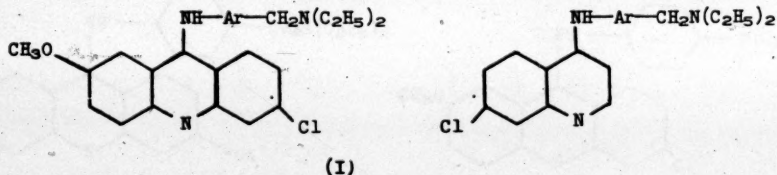
CHEMICAL STRUCTURE AND PARASITICIDAL ACTIVITY

X. THE EFFECT OF STRUCTURAL FEATURES OF THE CYCLIC SIDE-CHAIN SUBSTITUENT UPON ANTIMALARIAL ACTIVITY OF QUINOLINE AND ACRIDINE DERIVATIVES

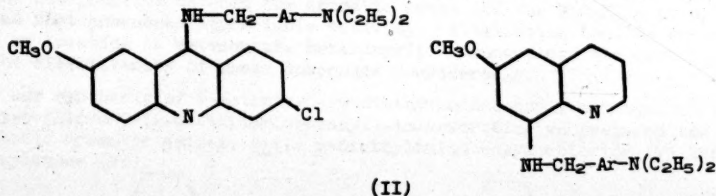
(THE PART PLAYED BY THE LOCATION OF THE METHYLENE GROUP)

V. I. Stavrovskaya

The substitution of an aliphatic-aromatic "cyclic side-chain substituent" for an aliphatic amine in acridine and quinoline antimalarials previously gave us substances of Type (I), which possessed appreciable antimalarial activity:



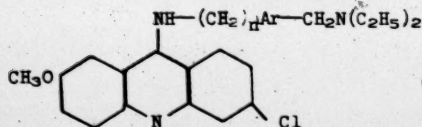
The present paper represents a continuation of this research on the synthesis of antimalarials with a "cyclic side-chain substituent". The following end products have been synthesized: 2-methoxy-6-chloro-9-(*m*-diethylamino-benzyl)-aminoacridine and 6-methoxy-8-(*m*-diethylaminobenzyl)-aminoquinoline may be classed as Type (II), with a CH_2 group located between the heterocyclic compound and the aromatic amine.



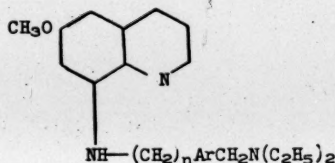
Tests of the quinoline derivative on *Pl. relictum* in siskins indicated that it possessed barely perceptible antimalarial activity, while the acridine derivative was inactive.

In a paper by Funke, Bovet, and Montezin [1], the authors describe a number of acridine and quinoline compounds of Type (III), in which we see that a $(\text{CH}_2)_n$ group is located between the aromatic ring and the heterocyclic one, with a CH_2 group between the aromatic ring and the $-\text{N}(\text{C}_2\text{H}_5)_2$ ($n = 1$ or 2):

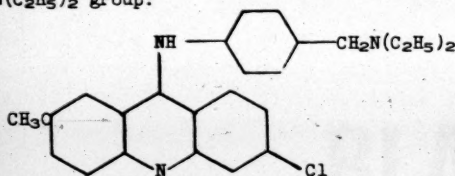
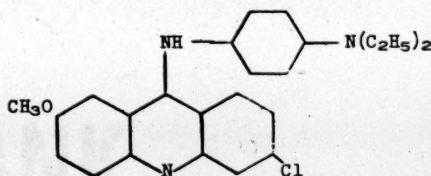
Most of these compounds display appreciable antimalarial activity, approaching that of atebirin.



(III)



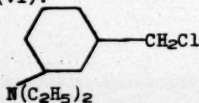
What is more, a comparison of Compounds SN 10.028 and SN 3.948 [2] [the latter may be classed as Type (IV)] demonstrates the great drop in antimalarial activity entailed by eliminating the CH_2 group between the aromatic ring and the $\text{N}(\text{C}_2\text{H}_5)_2$ group:

SN 10.028SN 3.948

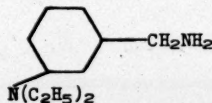
(IV)

Upon consideration of the structure of the substances we have synthesized, (I) and (II), and of the data in the literature cited, we see that the appreciable activity of these compounds is related to the replacement of the aliphatic amine by an aliphatic aromatic amine, rather than a purely aromatic one. Moreover, the location of the CH_2 group affects the degree of activity of these compounds: its position between the aromatic amine and the $\text{N}(\text{C}_2\text{H}_5)_2$ group yields a compound that possesses appreciable activity. Eliminating the CH_2 group at this position or locating it between the heterocyclic compound and the aromatic amine lowers the effectiveness of these compounds considerably.

For our synthesis of 6-methoxy-8-(m-diethylaminobenzyl)-aminoquinoline and 2-methoxy-6-chloro-9-(m-diethylaminobenzyl)-aminoacridine we prepared the respective aliphatic-aromatic amines, *viz.*: m-diethylaminobenzyl chloride (V) and m-diethylaminobenzylamine (VI):



(V)

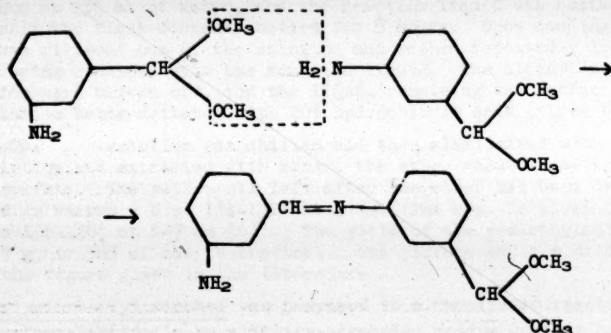


(VI)

In synthesizing (V) we started out with m-nitrobenzaldehyde dimethyl acetal, which we reduced to m-aminobenzaldehyde dimethyl acetal with sodium hydrosulfide.

Haworth and Lapworth [3] synthesized the latter product but did not give its constants. Nor are these figures to be found in the paper by Cocker and his associates [4], who used unrefined m-aminobenzaldehyde dimethyl acetal to synthesize m-diethylaminobenzaldehyde.

We tried to distil the resultant m-aminobenzaldehyde dimethyl acetal in vacuum. The substance began to decompose at about 70° at a vacuum of 6-7 mm, a volatile product that did not condense in the receiver being evolved rapidly, and the temperature and pressure continuously varying over a wide range. Then a small quantity of a yellowish liquid was distilled, the residue in the flask thickening greatly and turning into an amber-colored transparent solid mass upon cooling. An effort to distil the secondary fraction was unsuccessful. This is not a thoroughgoing decomposition of m-aminobenzaldehyde dimethyl acetal, however, but rather its polycondensation with the splitting out of methanol, in accordance with one of the following possible reactions:



The reason underlying this conclusion is that a polymer of m-aminobenzaldehyde settled out when the product was dissolved in 10% hydrochloric acid and then alkalinized with a caustic soda solution, acetylation of the polymer with acetic anhydride [5] yielding m-acetaminobenzaldehyde, while processing the polymer with hydrochloric methanol reconverted it into m-aminobenzaldehyde dimethyl acetal. The identity of the latter substance was established by converting it into m-diethylaminobenzaldehyde.

We effected the further transformation of m-aminobenzaldehyde dimethyl acetal into m-diethylaminobenzaldehyde by heating it in aqueous alcohol for 8 hours with ethyl iodide over a water bath. This method is superior to that employed by Cocker and Harris [6], who agitated m-aminobenzaldehyde dimethyl acetal with ethyl sulfate in alkalinized ether for seven days. We secured m-diethylaminobenzylamine (VI) from m-diethylaminobenzyl chloride via the latter's phthalimide derivative, decomposing the latter with hydrazine hydrate.

We wish to express our gratitude to Prof. Sh. D. Moshkovsky and S. A. Syrkin for the biological tests they carried out.

EXPERIMENTAL

m-Nitrobenzaldehyde dimethyl acetal 24 g of m-nitrobenzaldehyde was dissolved in 120 ml of methanol and 1% HCl and allowed to stand at room temperature for 6 days, after which the liquid was poured into a 2% solution of sodium hydroxide and extracted with ether. The ethereal solution was decanted with potash. The residue left after the ether had been driven off was vacuum distilled at 162-163° at 19 mm. The product totaled 26.7 g. The yield was 85%.

m-Aminobenzaldehyde dimethyl acetal was synthesized by reducing m-nitrobenzaldehyde dimethyl acetal with sodium hydrosulfide [4]. The m-nitrobenzaldehyde dimethyl acetal (12 g) was added a drop at a time to a heated solution of sodium sulfide (40 g) in 40 ml of water and 20 ml of hydrochloric acid (sp.gr.1.19). After the drop-by-drop addition was over, the reaction liquid was boiled for 6 hours, allowed to cool, and extracted with ether. The ether solution was washed with water and desiccated with potash. Driving off the ether left a reddish-yellow oil totaling 10.8 g.

m-Diethylaminobenzaldehyde. An alcoholic solution (150 ml) of m-aminobenzaldehyde dimethyl acetal (20.5 g) and ethyl iodide (36 g) was added to a solution of 35 g of soda in 135 ml of water, and the reaction liquid was heated over a water bath until the flask contents boiled for 8 hours. Upon cooling, the mineral precipitate was filtered out of the solution and washed repeatedly in alcohol, the wash alcohol being combined with the reaction liquid. The alcohol and the unreacted ethyl iodide were driven off, and the liquid remaining was extracted with ether, the ether solution being agitated with 20% hydrochloric acid (three 60-ml batches).

The H_2SO_4 solution was chilled and then alkalized with 10% sodium hydroxide solution and extracted with ether, the ether solution being desiccated with sodium sulfate. The yellow oil left after the ether had been driven off was distilled in vacuum - b.p. $131-132^\circ$ at 5 mm. (The b.p. is given in the literature as $136-138^\circ$ at 6-7 mm [6]). The yield of the m-diethylaminobenzaldehyde was 12.7 g, or 58% of the theoretical. The picrate had a m.p. of 146° , which agrees with the figure given in the literature.

m-Diethylaminobenzyl alcohol was prepared in a Cannizzaro reaction from m-diethylaminobenzaldehyde in an alkaline-alcoholic medium containing formaldehyde. A solution of m-diethylaminobenzaldehyde (15.4 g) in 100 ml of alcohol was combined with 12 ml of formalin and a solution of potassium hydroxide (27 g) in 30 ml of water, with constant stirring. The temperature rose from 10 to 14° . The solution was then poured into a cylinder with a ground-glass stopper, shaken up energetically, and kept in a 40° water bath for one hour, after which the liquid was poured into 250 ml of water and extracted with ether, the ether solution being desiccated with sodium sulfate. The yellow oil left after the ether had been driven off was distilled in a vacuum of 3 mm at 135° . The yield was 13.0 g, or 83% of the theoretical. m-Diethylaminobenzyl alcohol is a yellowish liquid that is freely soluble in alcohol, benzene, ether, and acids, though insoluble in alkalis or water.

7.978 mg substance: 0.568 ml N_2 (24° , 736 mm). 6.594 ml substance: 0.470 ml N_2 (22° , 732 mm). Found %: N 7.92; 7.94. $C_{11}H_{17}ON$. Calculated %: N 7.82.

m-Diethylaminobenzyl chloride (V) was synthesized from m-diethylaminobenzyl alcohol and phosphorus pentachloride. 18 g of phosphorus pentachloride was added a little at a time to 15.4 g of m-diethylaminobenzyl alcohol, a violent reaction resulting, with considerable warming of the reaction mass, which died down toward the end of the addition. After all the phosphorus pentachloride had been added, the liquid was heated over a boiling water bath for an hour. When the reaction mass had cooled, pieces of ice were added, and the aqueous solution was alkalized with ammonia until an oily product settled out. The latter was extracted with ether, the ether solution being washed with water and desiccated with sodium sulfate. The liquid left after the ether had been driven off was distilled at 120° in a 3-mm vacuum. The yield was 11 g, or 64% of the theoretical.

m-Diethylaminobenzyl chloride is a light-yellow oil with an aromatic fragrance, which is freely soluble in alcohol, ether, benzene, and acids, but is insoluble in

water or alkalis.

6.037 mg substance: 0.392 ml N_2 (22°, 737 mm). 3.485 mg substance: 0.235 ml N_2 (24°, 738 mm). Found %: N 7.29, 7.53. $C_{11}H_{18}NCl$. Calculated %: N 7.11

The picrate consisted of minute rhombohedrons with a m.p. of 111-112° after crystallization from alcohol.

3.441 mg substance: 0.412 ml N_2 (24°, 732 mm). 3.960 mg substance: 0.481 ml N_2 (23°, 739 mm). Found %: N 13.25, 13.62. $C_{17}H_{18}O_7N_4Cl$. Calculated %: N 13.14.

Distillation of m-diethylaminobenzylchloride at an insufficient vacuum or at too high a temperature results in partial decomposition of the product. The hydrogen chloride evolved reacts with the base to form the hydrochloride of m-diethylaminobenzyl chloride, which settles out as white crystals that float on the liquid base in the receiver. The hydrochloride was likewise secured by passing anhydrous hydrogen chloride through a solution of the base in ether or through the base directly, no solvent being used. It is freely soluble in alcohol, soluble in water (turning the solution cloudy), and insoluble in ether. M.p. 124°.

6-Methoxy-8-(m-diethylaminobenzyl)-aminoquinoline. m-Diethylaminobenzyl chloride (10.1 g) was heated over an oil bath with 6-methoxy-8-aminoquinoline for 8 hours at 134-145°. Upon cooling the solidified mass was dissolved in water, and the filtered solution was alkalized with a 10% solution of sodium hydroxide. The thick, brown oil that settled out was extracted with ether, and the ether solution was desiccated with potash. The residue left after the ether had been driven off was distilled in vacuum. The initial fraction, collected at 170-230° and 5-6 mm, consisted principally of the unreacted 6-methoxy-8-aminoquinoline (2.5 g). The second fraction, collected at 235-245° and 3 mm, was the base 6-methoxy-8-(m-diethylaminobenzyl)-aminoquinoline. The yield was 6.7 g (39% of the theoretical).

The base is a very thick, slightly yellowish oil, displaying green fluorescence, that darkens rather quickly when exposed to the air. It is freely soluble in alcohol, benzene, ether, and acids but is insoluble in water or alkalis.

4.785 mg substance: 0.549 ml N_2 (24°, 737 mm) 4.559 mg substance: 0.529 ml N_2 (24°, 737 mm). Found %: N 12.79, 12.93. $C_{21}H_{25}N_3O$. Calculated %: N 12.54.

The orange dipicrate had a m.p. of 160°.

3.779 mg substance: 0.549 ml N_2 (24°, 739 mm). 2.519 mg substance: 0.363 ml N_2 (24°, 739 mm). Found %: N 16.23, 16.10. $C_{33}H_{31}O_{15}N_9$. Calculated %: N 15.89.

m-Diethylaminobenzylphthalimide. A well-mixed mixture of phthalimide (14.7 g), m-diethylaminobenzyl chloride (19.7 g), and potash (6.9 g) was heated to 180-185° for 4 hours over an oil bath. The reaction mass was distilled with steam to drive off the unreacted substances. The thick dark-brown substance remains within the flask was extracted with ether, and the ether solution dried with sodium sulfate. Driving off the ether left 29 g of a thick brown product, which was distilled at 238-242° in a 3-mm vacuum. The yield was 24.8 g, or 80.5% of the theoretical.

The slightly mobile yellowish-red liquid slowly thickened when kept in a vacuum desiccator. m-Diethylaminobenzylphthalimide is freely soluble in alcohol, benzene, and acetic acid.

6.206 mg substance: 0.490 ml N_2 (18°, 754 mm). 6.288 mg substance: 0.519 ml N_2 (20°, 753 mm). Found %: N 9.19, 9.53. $C_{19}H_{21}O_2N_2$. Calculated %: N 9.06.

m-Diethylaminobenzylamine (VI). Hydrazine hydrate (5 g) was added to a solution of m-diethylaminobenzylphthalimide (10.3 g) in 20 ml of absolute alcohol, and

the reaction liquid was heated for an hour over a boiling water bath. A yellowish solid began to separate out, its bulk gradually increasing. When heating was complete, the alcohol was driven off, and 20% hydrochloric acid (40 ml) was added to the residue in the flask, the liquid then being boiled for one hour. The resultant phthalyl hydrazide was filtered out and washed with water. The filtrate was alkalized with 40% sodium hydroxide solution and extracted with ether, the ether solution being desiccated with potash. Driving off the ether left 9.2 g of a thick dark liquid. The latter was distilled at 123-130° in a 2-3 mm vacuum, the distillate totaling 3.4 g. There remained in the flask 3.8 g of a thick dark substance, which proved to be the unreacted *m*-diethylaminobenzylphthalimide. The first fraction was redistilled at 122-123° and 2-2.5 mm, the yield being 2.9 g, or 50% of the theoretical. The base is a mobile reddish-yellow liquid that is freely soluble in alcohol, ether, benzene, and dilute acids; it is insoluble in alkalis or water.

5.263 mg substance: 1.735 ml N₂ (20°, 748 mm) 3.428 mg substance: 0.480 ml N₂ (20°, 748 mm). Found %: N 16.01, 16.06. C₁₁H₁₈N₂ Calculated %: N 15.73.

The hydrochloride is yellow. It crystallizes from absolute alcohol as hexagonal platelets. M.p. 240° with decomposition.

3.883 mg substance: 0.392 ml N₂ (20°, 736 mm). 3.891 mg substance: 0.392 ml N₂ (19°, 734 mm). Found %: N 11.39, 11.37. C₁₁H₂₀N₂Cl₂. Calculated %: N 11.16.

The picrate, minute lemon-yellow prisms, crystallized from alcohol. M.p. 145-146°.

6.812 mg substance; 1.039 ml N₂ (20°, 744 mm). 3.725 mg substance: 0.588 ml N₂ (16°, 730 mm). Found %: N 17.40, 17.91. C₁₁H₂₄O₄N₂. Calculated %: N 17.61.

2-Methoxy-6-chloro-9-(*m*-diethylaminobenzyl)-aminoacridine was prepared in the usual manner from 2-methoxy-6,9-dichloroacridine (2.8 g) and *m*-diethylaminobenzylamine (2 g) in phenol (15 g). The yellow base was crystallized as thin platelets from alcohol. M.p. 104°. Soluble in alcohol, ether, acetone, and acids; insoluble in water.

4.743 mg substance: 0.421 ml N₂ (20°, 749 mm). 4.967 mg substance: 0.441 ml N₂ (20°, 749 mm). Found %: N 10.19, 10.19. C₂₃H₂₆ON₃Cl. Calculated %: N 10.01.

The yellow dihydrochloride crystallized from absolute alcohol as fine needles, having a m.p. of 252-254° with decomposition.

5.612 mg substance: 0.421 ml N₂ (22°, 728 mm). 5.495 mg substance: 0.412 ml N₂ (20°, 736 mm). Found %: N 8.31, 8.46. C₂₅H₂₈ON₃Cl₃·H₂O. Calculated %: N 8.23.

SUMMARY

1. The considerable antimalarial activity of compounds of Types (I) and (III) is due to the replacement of the aliphatic amine by an aliphatic-aromatic amine.
2. The presence of a CH₂ group between the aromatic amine and the N(C₂H₅)₂ group yields a substance that possesses appreciable antimalarial activity.
3. Removing the CH₂ group from this position or placing it between the heterocyclic ring and the aromatic amine reduces the effectiveness of these compounds considerably.

LITERATURE CITED

- [1] A. Funke, D. Bovet, J. Montezin, Ann. Inst. Pasteur, 72, 264 (1946).

[2] Survey of Antimalarial Drugs, 1941-1945 ed Wiselogle, pp. 1355, 1367.

[3] R.Haworth, A.Lapworth, J.Chem. Soc., 1922, 76.

[4] W.Cocker, J.O.Harris, J.V.Loach, J. Chem. Soc., 1938, 751.

[5] P.Friedlander, K.Fritsch, Monatsh., 24, 3 (1903).

[6] W.Cocker, J.O.Harris, J.Chem. Soc., 1939, 1093.

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Received September 15, 1949.

THE SYNTHESIS OF SOME HOMOLOGS OF THE AGLUCONES OF CARDIAC GLYCOSIDES.

I. SYNTHESIS OF TWO ISOMERIC β -PHENANTHRYL- $\Delta^{\alpha-\beta}$ -BUTENOLIDES¹⁾

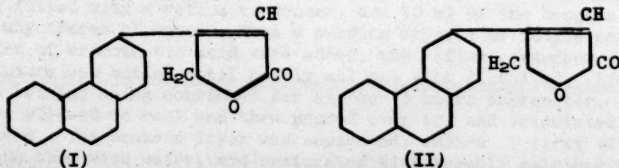
S.I.Kanevskaya and K.I.Znaeva

One of the principal results of many years of research on the chemistry of the cardiac glycosides has been the establishment of the fact that their aglucones have a structure that constitute them a special group of steroids whose pharmacological and chemical properties are due to the special structure of their side chain. As we now know, the latter is a $\Delta^{\alpha-\beta}$ -butenolide, with the polycyclic system of perhydrocyclopentanephenanthrene attached at the β -position. These facts, which have been elucidated extensively in several survey papers published in 1934-1936 [1, 2, 3], as well as quite recently [4,5], have served as the foundation for the developments characterizing research in this interesting field during the last few years: synthetic research. This research is proceeding along two lines: on the one hand, analogs and homologs of the steroid type are being synthesized, and on the other, simpler homologs are being synthesized, containing single ring or two-ring radicals that constitute part of the complicated cyclopentanephenanthrene system, so to speak, as substituents at the β -position of the butenolide. These homologs include, by way of example, phenyl, cyclohexyl, naphthyl, and indanyl derivatives (cf [4]).

But among all these substituted derivatives of the $\Delta^{\alpha-\beta}$ -butenolides we do not find phenanthrene derivatives; what is more, by analogy with other natural phenanthrene compounds, we ought to expect to find compounds here that are highly interesting pharmacologically. We were interested in filling this gap.

We therefore planned the synthesis of a series of $\Delta^{\alpha-\beta}$ -butenolides, containing the phenanthrene radical as such as well as in various stages of hydrogenation and hydroxylation, by analogy with the natural aglucones as a substituent. Comparative pharmacological testing of all these compounds would enable us to learn the extent to which the completeness of the perhydrocyclopentanephenanthrene system is necessary for producing the specific effect of cardiac glycosides.

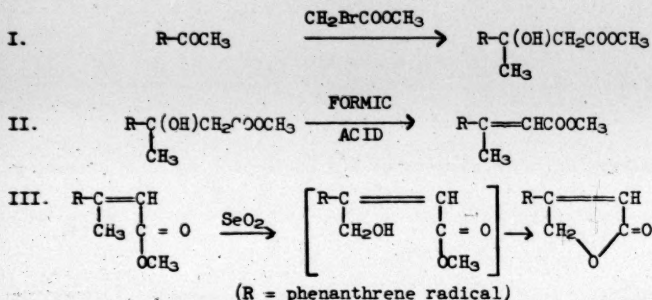
The present paper deals with the synthesis of two such isomeric butenolides of the phenanthrene series, namely β -(2-phenanthryl)- and β -(3-phenanthryl)- $\Delta^{\alpha-\beta}$ -butenolides (I) and II):



They have been synthesized by a method developed simultaneously and independently by two schools [6,7]. The initial substances used were the respective β -phenanthryl- β -methylacrylic acids. It has been learned that when β -methylacrylic acids are oxidized with selenium dioxide, the methyl radical is oxidized to the alcohol, the respective $\Delta^{\alpha-\beta}$ -unsaturated lactones being formed at the very instant of the reaction. We synthesized the β -phenanthryl- β -methylacrylic acids

¹⁾ Presented at the Scientific Council of the Institute in 1947.

required for this synthesis from the corresponding acetylphenanthrenes by the method evolved by Bergmann and his associates [8], viz: a β -hydroxy acid was prepared from acetylphenanthrene by a Reformatsky reaction, the acid being converted into the corresponding acrylic acid via dehydration with formic acid. Thus the synthesis as a whole may be depicted as follows:



The reaction is fairly smooth in all its stages, though the recovery of the end products involves considerable difficulty, its success requiring chromatography with aluminum oxide, followed by elutriation with chloroform.

In the pure state, both of the isomeric butenolides (I) and (II) are well crystallized substances that give a positive Legalle reaction like the natural aglucones, are relatively readily soluble in the usual solvents, insoluble in water, and fairly well soluble in saturated aqueous solutions of some salts of organic acids.

These solutions were submitted for testing to the pharmacological laboratory of the All-Union Research Institute of Pharmaceutical Chemistry, headed by Dr. M. D. Mashkovsky, to whom we are deeply indebted. These tests showed that neither of the synthesized lactones acted upon heart muscle.

EXPERIMENTAL

I. Synthesis of β -(3-Phenanthryl)- $\Delta^{\alpha\beta}$ -butenolide (II).

1. Preparation of the methyl ester of β -(3-phenanthryl)- β -methylacrylic acid.

3 g of acetylphenanthrene, prepared from phenanthrene by the Mosetig and Van de Kamp method [9], 1-2 g of coppered zinc (in the form of chips), and 45 ml of anhydrous benzene distilled with metallic sodium were placed in a small round-bottomed flask fitted with a reflux condenser, and 10 ml of the benzene was driven off to remove any traces of water. Then a seeding crystal of iodine and 2.3 g of the methyl ester of bromoacetic acid were added, the reflux condenser was connected, and the mixture was boiled until nearly all the zinc dissolved, which required 3-4 hours, heating being continued for another 3 hours thereafter. The reaction mixture was allowed to cool and then poured over ice and acidulated with 10% sulfuric acid. The benzene layer was separated, washed first with a 5% soda solution and then with water, and desiccated with freshly calcined sodium sulfate. Driving off the benzene left behind 3.8 g of a viscous, dark-brown mass. As measurement of the saponification number indicated, this mass, which did not crystallize even when allowed to stand for a long time, was the nearly pure methyl ester of β -(3-phenanthryl)- β -methyl- β -hydroxyhydracrylic acid, which was used to synthesize the desired acrylic acid without further purification. This was done by adding 11-12 g of 80% of formic acid to the reaction product, and

the whole was heated over an oil bath to the temperature at which the reaction mixture boiled (bath temperature 140-150°). Then the chilled mixture was poured into water, the resultant oil being extracted with ether, to which a slight amount of chloroform had been added to effect better solution. The resultant ether-chloroform solution was desiccated with freshly calcined sodium sulfate; driving off the solvent yielded 3 g of a thick dark-reddish oil that did not crystallize.

Since, as far as we know, the acid and its derivatives corresponding to this ester have not been described in the literature, and since we were unable to crystallize the resultant ether or to purify it by distillation, we endeavored to isolate it by saponification with acid and identify it as its silver salt. This was done by saponifying 1 g of the resultant oil by boiling it for 2 hours over a water bath with a 1N alcoholic solution of potassium hydroxide. Then it was accurately neutralized with a 0.1 N solution of hydrochloric acid, 0.25 g of a precipitate being thrown down (m.p. 57-72°), which we did not investigate. After the precipitate had been filtered out, the neutral solution was evaporated over a water bath; and the residue was dissolved in water, filtered, and acidulated with dilute sulfuric acid until its reaction was acid with Congo red, a white caseous precipitate of the acid, with a m.p. of 72-85°, being thrown down. The resultant acid was purified by repeated dissolution in alkali, followed by precipitation in sulfuric acid, after which it was identified as the silver salt. The latter was prepared by dissolving the purified acid in an excess of ammonia; the excess of the latter was eliminated by heating over a water bath and the solution was precipitated with silver nitrate, the resultant cream-colored precipitate was filtered out, thoroughly washed with water and desiccated in the dark in a desiccator above phosphoric anhydride. Analysis of this precipitate showed that it was the pure silver salt of β -(3-phenanthryl)- β -methylacrylic acid.

0.1218 g substance: 0.0354 g Ag. Found %: Ag 29.06. $C_{18}H_{13}O_2Ag$. Calculated %: Ag 29.23.

2. Oxidation of the methyl ester of β -(3-phenanthryl)- β -methylacrylic acid and preparation of β -(3-phenanthryl)- $\Delta^{\alpha-\beta}$ -butenolide. 0.5 g of the unpurified ester synthesized above and 30 g of freshly distilled acetic anhydride were placed in a small round-bottomed flask fitted with a reflux condenser and heated to boiling, and a solution of 0.4 g of freshly sublimed selenium dioxide in 2 ml of water. A black precipitate of reduced selenium appeared on the walls of the flask very soon. After heating had continued for 2 hours, the acetic anhydride was driven off in vacuum, the residue being dissolved in benzene, the selenium filtered out, and the benzene driven off in vacuum, leaving behind a light-brown oil, which crystallized partially after standing for a long time. The desired product was recovered by dissolving the reaction mixture in 20-30 ml of chloroform and chromatographed with alumina, the resultant solution being passed through a column 250 mm high and 15 mm in diameter. When the column was washed out with small batches of chloroform (30 ml each), a sharp brown zone appeared at the top of the tube. The chloroform was driven off, the first 6 fractions of the residue yielding a brown, non-crystalline oil; fractions 6 to 15 yielded light-yellow crystals that fused at 160-170°. They were collected (0.15 g) and recrystallized twice from a 1:1 chloroform-alcohol mixture, after which they exhibited a sharp m.p. of 177.5 - 178.5°, the positive Legalle reaction that is characteristic for aglucones of cardiac glycosides, and, as analysis showed, were the pure substance: β -(3-phenanthryl)- $\Delta^{\alpha-\beta}$ -butenolide.

3.610 mg substance: 10.999 mg CO_2 ; 1.616 mg H_2O . Found %: C 83.02; H 5.01. $C_{18}H_{12}O_2$. Calculated %: C 83.08; H 4.61.

II. Synthesis of β -(2-phenanthryl)- $\Delta^{\alpha-\beta}$ -butenolide (I)

This isomer was synthesized in the same way as the preceding one, the initial substance employed being the methyl ester of β -(2-phenanthryl)- β -methylacrylic acid, which we synthesized from 2-acetylphenanthrene by the Bergmann and Hillemann method [8].

0.4 g of this acid was heated to boiling with 30 g of acetic anhydride in a small round-bottomed flask fitted with a reflux condenser, and 0.4 g of freshly sublimed selenium dioxide dissolved in 2 ml of water added to the boiling solution. After boiling had gone on for 2 hours, the acetic anhydride was driven off in vacuum, the residue was dissolved in boiling benzene, and the metallic selenium was filtered out. The benzene solution was again evaporated in vacuum, the residual reddish-brown oil being dissolved in chloroform and chromatographed with alumina. In the ensuing washing with chloroform (using 30 ml for each fraction), the fractions from 5-6 to 13 yielded a light-yellow solution; driving off the solvent yielded light-yellow crystals with a m.p. of 196-198°. The crystals were combined and recrystallized from benzene, after which they fused at 199-200° and exhibited a pronounced Legalle reaction.

3.137 mg substance: 9.571 mg CO₂; 1.270 mg H₂O. 2.350 mg substance: 7.159 mg CO₂; 0.969 mg H₂O. Found %: C 83.21, 83.08; H 4.5, 4.61. C₁₈H₁₂O₂. Calculated %: C 83.08, H 4.61.

SUMMARY

Two isomeric β -phenanthryl- $\Delta^{\alpha-\beta}$ -butenolides have been synthesized. The resulting compounds, like the aglucones of the cardiac glycosides, give a positive Legalle reaction, but do not exhibit the physiological action of the cardiac glycosides.

LITERATURE CITED

- [1] Tschesche, *Angew. Chem.* 47, 729, 1934.
- [2] Elderfield, *Chem. Rev.*, 17, 187 (1935).
- [3] Fieser. The Chemistry of Phenanthrene Derivatives, p. 387-453, Russ. ed. State Scientific and Technical Chemical Press (1941).
- [4] Kanevskaya and Madaeva, Chem. Prog. 15, 178-202 (1946).
- [5] R.B. Turner, *Chem. Rev.*, 43, 1-43 (1948).
- [6] Terrey, Cuck, Elderfield, *J. Org. Chem.*, 6, 289, 1948.
- [7] Ruzicka, Plattner, Pataki, *Helv. Acta.* 25, 425 (1942).
- [8] Bergmann, Hillemann, *Ber.*, 66, 1302 (1933).
- [9] Mosetig, Van de Kamp, *J. Am. Chem. Soc.*, 52, 3704 (1930).

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Received November 2, 1949.

RESOLUTION OF THE CONFERENCE ON THE THEORY OF CHEMICAL
STRUCTURE IN ORGANIC CHEMISTRY

(Adopted by the Conference on the Theory of Chemical Structure in
Organic Chemistry held in Moscow, June 14, 1951).

The Conference on the Theory of Chemical Structure in Organic Chemistry convened by the Division of Chemical Sciences of the USSR Academy of Sciences recognizes the great importance of the problems under discussion and engaging the attention of the entire chemical world of our country. The conference was attended by more than four hundred chemists, physicists, and philosophers from the USSR Academy of Sciences, and from the academies of the various republics, research institutes, and institutions of higher learning of the Soviet Union.

The activity displayed by those attending the conference was a striking indication of its timeliness and of the need for its convening, as well as of the urgency of the problems under discussion. The inadequate attention paid by our country's chemists and physicists to the battle for the Weltanschauung of dialectical materialism in chemistry and in the related branches of physics, theoretical chemistry, and especially organic chemistry have resulted in some Soviet chemists falling prey to the defective idealistic "theory" of resonance.

The participants in the conference subjected the sterile "theory" of resonance and the errors of those Soviet scientists who expounded and employed this faulty concept in their work to devastating criticism. The conference clearly demonstrated the unshakability of the theory of the structure of organic compounds originated by the great Russian scientist A.M. Butlerov, which is the foundation of all of modern organic chemistry. The conference indicated the urgent necessity of further development of A.M. Butlerov's materialist theory of the structure of organic compounds and of a thorough study of the works of A.M. Butlerov and of the outstanding representatives of the famous Butlerov school of organic chemists.

In its discussion of the report by the Commission of the Division of Chemical Sciences of the USSR Academy of Sciences, the conference noted that a mighty industry of heavy chemical synthesis has been established during the Stalinist Five-Year Plans under the guidance of the party and the government and of Comrade Stalin himself: the first synthetic rubber industry in the world was established; and industries producing motor fuel, synthetic fiber, dyes, plastics, and so forth have been built up. Major successes have been achieved in recent years in the production of complicated organic preparations, filling the requirements of public health, and of the food, textile and other industries. The production of antibiotics, antimalarials, antituberculosis drugs, and other therapeutic preparations, flotation reagents, photosensitizers, insecticides, fungicides, and the like has been organized.

The conference notes that the achievements of the organic chemical industry are dependent upon the creative development of organic chemistry in our country. Discoveries such as Zelinsky's dehydrogenation catalysis, Kazansky's and Moldavsky's dehydroaromatization of the paraffins, Favorsky's isomeric transformations of unsaturated hydrocarbons, the Demyanov, Nametkin, Kizhner, and Arbuzov rearrangements, the Lebedev, Rodionov, and Nesmeyanov reactions, and many others, together with major theoretical generalizations, have made invaluable contributions to organic chemistry.

The conference notes that the creative trends in the theory of chemical structure have been paralleled by erroneous views that distorted the Butlerov theory. The name of Butlerov has been ignored in several monographs and textbooks on inorganic chemistry and molecular structure, and the significance of the work of Russian chemists in the development of theoretical organic chemistry has been deprecated. During recent years the so-called "theory" of resonance (of Pauling) or of mesomerism (Ingold) developed by Anglo-American scientists has received widespread currency in organic chemistry. This "theory," which teaches the multiform nature of a molecule's structure, contradicts the fundamental assumptions of Butlerov's theory.

Unfortunately, the concept of resonance or mesomerism, methodologically defective, physically groundless, and sterile, has found adherents and disciples among Soviet scientists (Ya. K. Syrkin, corresponding member of the USSR Academy of Sciences, M. E. Dyatkina, M. V. Volkenshtein, A. I. Kiprianov, and others). These scientists, propagandizing the idealistic and mechanistic concept of resonance, have endeavored to conceal the faultiness of this concept by claiming that it stems from quantum mechanics and is therefore competent to explain all the facts and behavior patterns in chemistry. The "theory" of resonance or mesomerism was likewise uncritically adopted by other Soviet scientists mentioned in the report. The spread of this "theory" has harmed Soviet chemistry. It has deflected the efforts of chemists toward useless pseudoscientific constructions, created the destructive illusion of elucidating many facts and patterns of behavior that actually remained unexplained, and tried to create the appearance of well-being in the evolution of chemical structure while actually retarding its development.

The conference notes that Ya. K. Syrkin, M. E. Dyatkina, M. V. Volkenshtein, A. P. Kiprianov, and others now acknowledge the erroneousness and sterility of this "theory." The conference notes, however, that in their remarks in the present discussion Ya. K. Syrkin, M. E. Dyatkina, M. V. Volkenshtein, and A. I. Kiprianov have not made a comprehensive critique of the resonance or mesomerism "theory" nor made a detailed analysis of their serious methodological and ideological errors. The conference considers that the declarations by Ya. K. Syrkin and M. V. Volkenshtein that they had not known of A. M. Butlerov's researches when they were writing their monographs on the nature of the chemical bond and molecular structure are unsatisfactory.

One of the major factors facilitating the spread of the idealistic "theory" of resonance in Soviet scientific literature has been the inadequate development of scientific criticism among Soviet chemists, who did not see through the ideological defectiveness of this concept and did not pay enough attention to problems of the methodology of Soviet chemical science. The resolution of the Central Committee of the Communist Party of the Soviet Union on ideological problems drew the attention of the Soviet chemical world to the problems of the science's methodology and aided in disclosing the existing errors in chemistry and in outlining the path of further development of chemical science, based on the only correct *Weltanschauung* of dialectical materialism. The conference notes the insufficient attention paid by Soviet philosophers to the methodological problems of theoretical chemistry, which has been manifested, in particular, by the fact that the idealism of the resonance concept was first exposed by the chemists and not by the philosophers.

The conference approves the basic principles of the report submitted by the Commission of the Division of Chemical Sciences of the USSR Academy of Sciences, which analyzes the present state of the theory of chemical structure, points out the idealistic nature of the "theory" of resonance and mesomerism, reveals the mistakes of some Soviet scientists, and charts the future development of the Butlerov theory.

The conference also considers it necessary to point out some major deficiencies in the Commission's report. The report does not show that the ideological distortions in matters of chemical theory are closely linked to hostile theories in biology and physiology, constituting a united front in the struggle of reactionary bourgeois ideology against materialism. It provides an incomplete characterization of the achievements of Soviet organic chemistry and fails to devote enough attention to the kinetics of chemical processes, the influence of the medium, and the nature of chemical reagents. Not enough light is shed on the chemistry of free radicals or on the mechanism involved in the highly important intramolecular re-arrangements. The report deals with only the best-known types of interaction between atoms within a molecule, which hardly exhaust the great diversity of this phenomenon. Nor can the terminology employed for some kinds of interaction be regarded as definitely established.

The conference considers that work on the development of the theory of organic chemistry must be expanded in every way. Synthesis is the leading branch of organic chemistry, together with the related researches on the structure and properties of organic substances (including natural ones) by the methods of synthetic organic chemistry. It is in chemical synthesis that the bond between theory and practice is most strikingly evident. Moreover, it is in synthetic research that the theory of structure is continuously tested and developed, and the field of its application expanded. The theory of structure also finds new stimuli for further development in synthetic research.

The conference is of the opinion that the most important objective of theoretical organic chemistry is the creative development of Butlerov's doctrine, deepening and extending its fundamental postulates in the light of contemporary concepts of the structure of matter. The evolution of theoretical organic chemistry and, most of all, the evolution of the theory of chemical structure must entail a resolute struggle against idealistic and mechanical theories in chemistry, based upon the Weltanschauung of dialectical materialism.

The attention of Soviet scientists must be focussed upon obtaining a deeper and more extensive knowledge of the chemical structure of matter and upon developing the theory of the interactions between atoms in a molecule. The problems of the reactivity of molecules as functions of their structure and of the medium must be solved. Research on elementary processes and on reaction kinetics and mechanisms, including catalytic reactions, is of extremely great importance. Research on the chemical, physical, physiological, and other properties of organic substances as functions of their structure is likewise one of the most important tasks ahead.

Solving the problems of theoretical organic chemistry will require the wider employment of all the achievements of the adjacent disciplines, most of all contemporary physics, with all its wealth of experimental and theoretical methods - this in addition to the chemical approaches and research methods that have proved their worth so brilliantly. In this connection the conference calls attention to the abnormal state of affairs in which many physicists refrain from participation in the struggle for the establishment of advanced theory in chemical science. Nor is it normal that hardly any of the leading theoretical physicists took part in the deliberations of the present conference.

The conference finds that physical research methods have not yet been utilized as much as they deserve in organic chemistry and holds that spectroscopic, electronographic, mass-spectrographic, and other methods must be widely employed in research on the structure and properties of organic compounds. The problems involved in the development of the theory of chemical structure require the

elaboration of the foregoing and of new physical and physico-chemical research methods, applied to the specific problems involved. The conference calls upon physicists and physical chemists to take an active part in the development of these methods.

The conference likewise takes note of the inadequate participation of theoretical physicists in the development of quantum chemistry. Soviet theoretical physicists and mathematicians must play an active part in working out the problems of theoretical chemistry and in developing computational methods in quantum mechanics. Only through the joint efforts of chemists and physicists can the theory of chemical structure be transformed into the quantitative theory called for by A.M. Butlerov.

The publication of more domestic monographs on theoretical problems in chemistry must be expanded. One of the most important objectives must be the preparation and publication of new textbooks of organic chemistry that set forth the present state of chemical science correctly. The publication of the works of our native classics, already under way by the Division of Chemical Sciences, must be sped up, with emphasis laid upon the complete collected works of A.M. Butlerov and V.V. Markovnikov.

The conference notes that the Division of Chemical Sciences of the USSR Academy of Sciences, as well as scientific institutes and institutions of higher learning, must pay more attention to theoretical chemistry and the problems involved in the ideological foundations of chemical theory and must combat the penetration of foreign idealistic theories into Soviet science more vigorously.

The conference recommends that:

1. The stenographic report of the conference be published as fast as possible (no later than the end of 1951).
2. The results of the conference be set forth in extenso in scientific journals.
3. Steps be taken to obtain publication of speeches made during the discussion of the development of the theory of chemical structure in organic chemistry, especially in the Journal of General Chemistry, increasing the number of pages in the journal for the occasion.
4. The publication of new textbooks of organic chemistry, correctly expounding the present state of chemical science, and of domestic monograph literature on theoretical problems in chemistry be accelerated.
5. The Division of Chemical Sciences of the USSR Academy of Sciences periodically convene conferences on the principal problems of organic chemistry, inviting scientists who are specialists in the adjacent disciplines (physicists, philosophers, biologists, and the like.)

The conference calls upon chemists, as well as the scientists working in the adjacent branches of physics, for further creative development of A.M. Butlerov's theory of chemical structure based upon dialectical materialism and guided by the brilliant works of J.V. Stalin and by his propositions regarding the role and the importance of advanced science in the evolution of society, and the role and importance of criticism in the development of science. The conference calls upon Soviet chemists for comprehensive development of theoretical chemistry, and the wide application of the results of scientific research in our national economy.

Under the leadership of the party of Lenin and Stalin Soviet chemists will honorably comply with the instructions of the great leader of the toilers, the scientist of genius, Joseph Vissarionovich Stalin.